WO9106035

Publication Title:

LIGHT-SENSITIVE RECORDING MEDIA

Abstract:

Abstract of WO9106035

Light sensitive recording media such as a silver halide photographic emulsion (10) or an optical recording disk or plate (50a or 50b). The photographic emulsion comprises a colloid or gel (12), and a multitude of silver halide particles (14) dispersed in that colloid. Each of these particles (16) includes at least a core (16a) surrounded by a shell (16b), one of the core and shell includes a silver halide (20c), and the other of the core and shell includes a dielectric (20a). The optical recording disk or plate comprises a solid, light reflecting or light transmitting substrate (52), a colloid (56) applied onto the substrate, and a multitude of particles (54), dispersed in that colloid. Each of these particles includes a core surrounded by a shell, and at least one of the core and shell consists essentially of a metal (20b).

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| (51) International Patent Classification [5] : G03C 1/00, 1/72, G11B 5/00 G11B 7/00, B05D 7/00 B32B 5/16, 9/00, 15/02 | A1 | (11) International Publication Number: WO 91/06035 |
| | | (43) International Publication Date: 2 May 1991 (02.05.91) |

(21) International Application Number: PCT/US90/06008

(22) International Filing Date: 18 October 1990 (18.10.90)

(30) Priority data:
422,728   18 October 1989 (18.10.89)   US

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(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: LIGHT-SENSITIVE RECORDING MEDIA
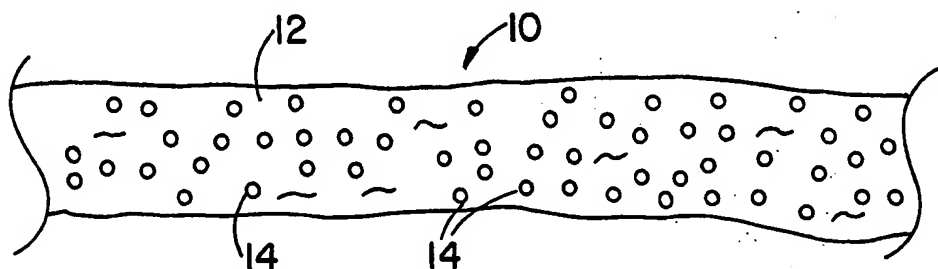
(57) Abstract

Light sensitive recording media such as a silver halide photographic emulsion (10) or an optical recording disk or plate (50a or 50b). The photographic emulsion comprises a colloid or gel (12), and a multitude of silver halide particles (14) dispersed in that colloid. Each of these particles (16) includes at least a core (16a) surrounded by a shell (16b), one of the core and shell includes a silver halide (20c), and the other of the core and shell includes a dielectric (20a). The optical recording disk or plate comprises a solid, light reflecting or light transmitting substrate (52), a colloid (56) applied onto the substrate, and a multitude of particles (54), dispersed in that colloid. Each of these particles includes a core surrounded by a shell, and at least one of the core and shell consists essentially of a metal (20b).

LIGHT-SENSITIVE RECORDING MEDIA

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BACKGROUND OF THE INVENTION

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This invention generally relates to light sensitive recording media such as a light-sensitive silver-halide emulsion.

Light sensitive recording media are used in many different applications; and, for example, light sensitive silver halide emulsions are often used as photographic

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emulsions. The requirements for a commercially successful photographic silver halide emulsion are quite severe. Among other needs, such emulsions must be highly sensitive, have fine grain, sharpness and abundant latitude, and have sufficiently high optical density and sufficiently low fog

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density. In addition, the emulsions must be highly processable, easy to develop and to wash, but at the same time, the emulsions must be able to hold or fix an image and be highly resistant to various chemical agents. Further, it is important that the photographic and processing properties

20
of the emulsions be stable over lengthy periods of time prior to use, that the quality of the emulsions be highly dependable and reproducible, and that the cost of producing the emulsions be low.

Numerous specific light sensitive emulsions are

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known that, to one degree or another, satisfy these requirements; and several known emulsions contain particles of silver halide dispersed as a colloid or in gel, with either the construction or properties of the particles being designed to improve or enhance the quality of the emulsions.

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For instance, U.S. Patent 4,484,877 discloses a light sensitive silver halide emulsion which comprises silver

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halide grains composed of a core and a shell. The core

1 consists essentially of silver halide containing silver
iodide, and the shell covers the core and consists
essentially of silver bromide, silver chloride or silver
chlorobromide. The shells have thicknesses from 0.01 to 0.1

5 micrometers.

U.S. Patent 4,728,602 discloses a light sensitive
silver iodobromide emulsion containing silver iodobromide
grains composed of a core and a shell. The core
substantially comprises silver iodobromide containing at

10 least about 5 mol percent of silver iodide; and the shell
substantially comprises iodobromide having a lower silver
iodide content than the silver iodobromide content of the
core, or the shell substantially comprises silver bromide.
The relative standard deviation of the silver iodide content

15 of the individual grains of the emulsion is lower than about
20 percent.

U.S. Patent 4,639,410 discloses a silver halide
color photographic light sensitive material including a
core-shell type silver halide emulsion. The shells in the

20 emulsion consist substantially of silver bromide, but they
may contain silver iodide, silver chloride or silver
iodochloride; and the core of each sphere is preferably
silver iodobromide, although it may contain a silver halide
other than silver iodobromide, such as silver chloride.

25　　　　All of these emulsions, as well as most or even all
other conventional silver halide photographic emulsions,
contain relatively large amounts of silver and color films
contain relatively large amounts of dyes and/or precursors of
dyes. Because of the high cost of silver, it is very

30 desirable to provide a silver halide photographic emulsion

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containing less silver and less dyes and dye precursors than

1 these conventional emulsions.

Light sensitive recording media are also used as optical disks or plates to record data. In such applications, a first light beam, referred to as a write

5 beam, is passed over the recording medium in a given pattern to alter the morphology of the recording medium over a path or selected areas, which thereby represents stored data. After this change in morphology, the portions of the recording medium that were exposed to the write beam are very

10 much less able to absorb light than are the portions of the recording medium that were not exposed to the write beam.

Another light beam, referred to as a read beam, of an intensity low enough so that it does not change the morphology of the recording medium, can then be passed over

15 that medium. The read beam is reflected or transmitted when it strikes a portion of the recording medium previously exposed to the write beam, while the read beam is absorbed when it strikes a portion of the recording medium not previously exposed to the write beam. In this way, the read

20 beam can be used to determine, or read, the data stored in the recording medium.

Heretofore, optical recording media were not made in a manner that takes advantage of the plasmon resonance effect, which is an effect that increases the intensity of

25 certain electromagnetic fields. In accordance with the present invention, it has been determined that optical recording media can be made that effectively employ the plasmon resonance effect to significantly improve the sensitivity of the recording media to light and other

30 electromagnetic radiation in the optical spectrum.

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The plasmon resonance effect is shown by certain
1 small particles and this effect includes the enhancement of
electromagnetic fields at certain frequencies inside and near
the particle, and the enhancement of the scattering,
absorption and extinction of certain frequencies of light.
5 The extinction is defined as the sum of the absorption and
scattering. The extent to which a particle exhibits the
plasmon resonance effect depends on a number of factors,
including the size and shape of the particle, the material or
materials from which the particle is made, and, in a particle
10 made of a plurality of materials, the order, number, shape
and dimensions of the materials from which the particle is
made. For example, the plasmon resonance effect may be
enhanced in particles that have sizes on the order of
magnitude of tens of nanometers, and thus are commonly
15 referred to as nanoparticles. Because of the above
considerations, nanoparticles that consist of a number of
materials are of special interest because they can be made to
exhibit an enhanced plasmon resonance effect in a selected
electromagnetic frequency range. One consequence of the
20 frequency dependence of the plasmon resonance effect, and
hence the frequency dependence of absorption and scattering,
is that the particles are colored and consequently can be
useful in color photography, color printing, color copying,
etc. Any frequency at which a particle exhibits the plasmon
25 resonance effect is referred to as a resonance frequency or a
plasmon resonance frequency of the particle.

It has been recognized for many years that the
plasmon resonance effect in small metal particles can be
responsible for absorption and scattering phenomena of
30 electromagnetic radiation.

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Recently Kerker et al. in _Phy_. _Rev_. _B_, _26_,

1 052-4062 (1982), have recognized that by designing composite nano particles comprised of metal and dielectric layers, the plasmon resonance can be greatly enhanced. This now makes it possible to use the effect in many processes from nonlinear

5 optics to photochemical catalysis.

Consider, for example, a spherically shaped nano particle suspended in a medium, and consisting of a spherical core made of a dielectric material surrounded by a shell made of a metal. When electromagnetic radiation of a wavelength

10 much longer than the size of the particle is incident on that particle, the radiation scattering coefficient, a_1, of the particle, including the effect thereon of the plasmon resonance effect, is given by the equation:

15
$$a_1 \cong 2/3 \ i\alpha \left[\frac{(e_2-e_1)(e_1-2e_2) + q^3(2e_2+e_3)(e_1-e_2)}{(e_2+2e_3)(e_1+2e_2) - q^3(2e_2-2e_3)(e_1-e_2)} \right]$$

where, $q = a/b$

$\alpha = 2\pi b/\lambda$

20
    i is the imaginary number, $\sqrt{-1}$,
    a is the radius of he core of the particle,
    b is the radius of the particle,
        is the wavelength of the incident electromagnetic
25   radiation,

    ε_1 is the dielectric constant of the core,
    ε_2 is the dielectric constant of the shell, and
    ε_3 is the dielectric constant of the surrounding
30   medium.

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In the computations for this patent application,
1 all the coefficients of any significant magnitude were
included. As mentioned above, optical recording media have
not previously been made so as to utilize fully the plasmon
resonance effect. Pursuant to the present invention, by
5 providing an optical recording medium with selected nano
particles, the plasmon resonance effect can be effectively
employed to enhance dramatically the photoprocesses that
occur in the media.

In the present invention, particles are designed
10 and made which use various features of the plasmon resonance
effect to improve and enhance photographic emulsions and the
photographic process. First, particles which enhance the
fields are used to increase the intensity in the silver
halide layer of the particles and hence to enhance the
15 sensitivity of the silver halide to a given intensity of light
incident upon the emulsion. Second, coated particles, which
enhance the absorption and scattering of light with a much
smaller amount of silver than required with solid silver
particles, are used to decrease the amount of silver needed
20 in photographic emulsions, prints and films made with silver.
Third, coated particles, which enhance the
frequency-dependent absorption and scattering, and hence are
colored, are used to decrease the amount of dyes needed in
photographic prints and films.

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SUMMARY OF THE INVENTION

An object of this invention is to provide enhanced
optical responses in light sensitive media.

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Another object of this invention is to reduce the
1 amount of silver needed in a light sensitive silver halide
emulsion.

Another object of this invention is to reduce the
amount of dyes and dye precursors needed in a light sensitive
5 emulsion.

Another object of the present invention is to use
silver halide coated dielectric particles in a light
sensitive recording medium.

A further object of this invention is to use
10 particles comprising silver halide coated dielectric cores in
a light sensitive silver halide emulsion, where those
particles also include a metal shell to enhance the
sensitivity of the silver halide to light.

Still another object of the present invention is to
15 utilize the plasmon resonance effect to enhance the
sensitivity of an optical recording medium.

Another object of this invention is to provide an
optical recording medium with a multitude of nanoparticles,
each of which is made to exhibit the plasmon resonance
20 effect, to enhance the photo processes that occur in the
recording medium.

These and other objectives are attained with light
sensitive recording media constructed according to the
present invention. With a first embodiment, the medium is a
25 light sensitive silver halide photographic emulsion,
comprising a colloid or gel, and a multitude of silver halide
particles dispersed in that colloid. Each of these particles
includes at least a core surrounded by a shell, one of the
core and shell includes silver halide, and the other of the
30 core and shell includes a dielectric. Preferably, one of the

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core and shell consists essentially of silver halide, the

1 other of the core and shell consists essentially of the
dielectric material, and this dielectric material is
substantially free of silver.

With a second embodiment, the recording medium is a

5 light sensitive optical recording disk or plate, comprising a
solid, light reflecting or light transmitting substrate, a
colloid applied onto the substrate, and a multitude of
particles dispersed in that colloid. Each of these particles
includes a core surrounded by a shell, and at least one of

10 the core and shell consists essentially of a metal.
Preferably, the other of the core and shell consists
essentially of a dielectric; and more specifically, the core
of each of these preferred particles consists essentially of
a dielectric material, and the shell of each of these

15 particles consists of a metal.

Further benefits and advantages of the invention
will become apparent from a consideration of the following
detailed description given with reference to the accompanying
drawings, which specify and show preferred embodiments of the

20 invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 diagrammatically illustrates a

25 photographic emulsion according to the present invention.

Figures 2-5 and 5A, which are not drawn to scale,
show particles that may be used in the emulsion of Figure 1.

Figures 6-11 show the light absorption efficiency
of solid silver spheres and silver coated silica spheres at

30 wavelengths of 355nm, 382nm, 414nm, 497nm, 621nm and 828nm
respectively.

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Figures 11a-11f show similar wavelength dependent
1   spectra observed in the scattering and extinction spectra.

Figures 12 and 13 show optical recording media also
according to the present invention.

Figures 14-27, which are not drawn to scale, show
5   various particles that may be used in the optical recording
media of Figures 12 and 13.

Figures 28-36 outline several processes that may be
used to form the particles shown in Figures 2-5 and 14-27.

Figure 37 is a transmission electron micrograph of
10   silver-coated silver bromide nanoparticles.

Figure 38 is a transmission electron micrograph of
silver coated silver bromide nanoparticle treated with
ammonia.

Figure 39 shows various optical extinction spectra
15   of silver coated silver bromide nanoparticles. (a) to (d) are
spectra of illuminated solutions of Ag, Br, and EDTA with
specific concentrations. In going from a to d the
illumination time increases. (e) typical spectrum observed
after the addition of ammonia to any of the above solutions
20   either untreated or treated with ammonia, which were measured
shortly after light exposure at different illumination times.

Figure 40 shows computed extinction efficiencies
for silver coated silver bromide nanoparticles. The diameter
of the core particle is 20 nm and the thickness of the silver
25   coats are indicated in nm. The spectrum marked solid is that
of a homogeneous 20 nm diameter silver sphere.

Figure 41 is an optical extinction spectra of a
measured silver coated silver bromide nanoparticle and two
computed spectra. The measured spectrum lies between the two
30   computed spectra. In the upper curve all of the silver is
assumed to come from the reduction of AgBr at the particle
surface.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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Figure 1 illustrates a first light sensitive recording medium 10 according to the present invention. This medium is a light sensitive silver halide photographic

5 emulsion, comprising a colloid or gel 12, and a multitude of silver halide particles 14 dispersed in that colloid. Figures 2-5 show four types of particles, referenced at 16, 20 and 22, and 24, respectively, that may be used in emulsion 10. Each of these particles includes at least a core

10 surrounded by a shell; and in each of these particles, one of the core and shell includes silver halide, and the other of the core and shell includes a dielectric material. Preferably, the one of the core and shell consists essentially of silver halide, the other of the core and shell

15 consists essentially of a dielectric material, and moreover, this dielectric material is substantially free of silver. For example, particle 16 consists of core 16a and shell 16b, the core consists essentially of a dielectric material.

The term "dielectric" material or core as used

20 herein, refers to a material which is a non-conductor or a semi conductor. The conductivity of the material may range from 0, but preferably as low as 10^{-40} to 10^6 mhos. In a preferred embodiment, the conductivity ranges from 10^{-40} to 10^5 mhos. In a most preferred embodiment, the conductivity

25 ranges from 10^{-30} to 10^4 mhos. Examples of dielectric material includes glass, silica, cadmium sulfide, gallium arsenide, polydiacetylene, lead sulfide, titanium dioxide, polymethylacrylate (PMMA), silver bromide, carbon fibers, copper sulfide, silver sulfide, and the like.

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The shell consists essentially of silver halide.

1   Further, with this particle, shell 16b is disposed immediately over and substantially completely covers core 16a.

    In particle 20, a metal coating such as silver,

5   copper, aluminum, gold or palladium is disposed between the dielectric core and the silver halide shell to increase the sensitivity of the silver halide to light. This increased sensitivity is caused by the plasmon resonance effect produced by the metal coating. More specifically, particle

10 20 consists of dielectric core 20a, metal coating 20b disposed immediately over and covering that core, and a layer of silver halide 20c disposed immediately over and covering layer 20b.

    If it is desired to use a layer of metal between

15 the dielectric core and the silver halide shell, it may be preferred, as is done in particle 22, to separate or space the metal from the silver halide to prevent interference in the development of the latent image. In particular, particle 22 consists of dielectric core 22a, a layer of silver 22b

20 disposed immediately over and covering core 22a, a layer of dielectric material 22c such as a polymer, disposed immediately over and substantially covering the silver layer, and shell 22d formed of silver halide disposed immediately over and substantially completely covering layer 22c.

25   It is not necessary to the present invention in its broadest sense that the dielectric material and the silver halide of the particles used in emulsion 10 form the core and shell of the particle, respectively, and Figure 5 shows a fourth particle 24 that may be used in emulsion 10 and which

30 comprises core 24a comprised of silver halide and shell 24b

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comprised of a dielectric material. With the particle 24
1   shown in Figure 5, it is also desirable for some emulsions to
provide the particle with a layer of metal (not shown) to
enhance the sensitivity of the silver halide of the particle;
and if this is done, to further provide the particle with a
5   still further coating of a dielectric material (also not
shown) between that metal layer and the silver halide core of
the particle to prevent interference in the development of
the latent image.

Coated nanoparticles can be designed and made which
10   use features of the plasmon resonance effect to improve
photographic emulsions. Plasmon resonances of nanoparticles
can be used to improve both the recording (writing) of an
image and the regeneration (reading) of the image. In the
next two paragraphs the ways in which plasmon resonant
15   particles can be used in photography are explained briefly.
A more detailed discussion follows.

When light from a scene illuminates a typical
silver halide photographic emulsion it generates very small
silver particles in the silver halide grains. The pattern of
20   small silver particles form a latent image. It is often
desirable to increase the sensitivity of an emulsion to
light, i.e, to make an emulsion in which a latent image can
be formed with less light. By replacing the solid silver
halide particles in an emulsion with coated nanoparticles
25   where there is a silver layer underneath the silver halide
layer, the sensitivity of the silver halide to light can be
enhanced. A layered particle having the appropriate
thicknesses of dielectric, silver, polymer, and silver halide
can have a plasmon resonant enhancement of the light in the
30   silver halide layer. The enhanced optical intensity induces

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the formation of more latent image centers in a plasmon
1   resonant particle than in solid silver halide particles
illuminated with the same light intensity. Hence, the
plasmon resonance effect can be used to increase the
sensitivity of a given amount of silver halide to light, and
5   can improve the recording of an image.

After a typical silver halide emulsion is exposed,
the small clusters of silver in the latent image act as
nucleation centers for the reduction of the rest of the
silver in the grain and/or silver from solution. In black
10 and white photography, the absorption and scattering by the
reduced silver is responsible for the image observed when
illuminated with light. In color photography, the reduction
of the silver is coupled to the generation of dyes. When
illuminated with white light, the dyes in the emulsion absorb
15 certain wavelengths and consequently the film transmits
and/or reflects the complementary wavelengths. The solid
silver particles generated after development in black and
white photographs can be replaced with silver coated
nanoparticles that use less silver to absorb and scatter more
20 light. The same volume of silver can be much more absorbing
when it is coated at the right thickness onto the surface of
a dielectric nanoparticle. So it is possible to reduce the
amount of silver required in the photograph. Also, the dyes
generated during development in a color photograph can be
25 replaced with plasmon resonant silver coated nanoparticles
that, when illuminated with white light, reflect and transmit
colored light. By replacing expensive dyes with coated
nanoparticles, the cost of film can be reduced. So, plasmon
resonant coated nanoparticles can be used to reduce the cost
30 of both color and black and white photographs.

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Particles must be designed to enhance those aspects

1   of plasmon resonance required for each particular purpose.
The next five paragraphs state in more detail the aspects of
plasmon resonance used in the coated nanoparticles, how these
aspects are used in light recording devices, and the

5   advantages of using particles having such resonances.
Improvements in recording the image are discussed in (1).
Improvements in reading or regenerating the image are
discussed in (2)-(4). Improved particles to absorb stray
light are discussed in (5). Emulsions combining some of the

10   particles are discussed in (6).

     (1) Coated nanoparticles having a plasmon resonant
enhancement of the light in the silver halide layer of an
emulsion can be used to increase the sensitivity of a given
amount of silver halide to a given incident intensity of

15   light. Such coated particles can be of use in recording an
image in either color or black and white photography. One
type of appropriate nanoparticle has a dielectric core, a
first coat of silver, a second coat of a polymer, and a third
coat of a silver halide. The thicknesses of the core and

20   coats must be chosen to enhance the light intensity at the
appropriate wavelength range in the silver halide layer. An
advantage of using these particles is an increased
sensitivity of the emulsion and a decreased requirement for
silver.

25   (2) Coated particles having a plasmon resonant
enhancement of the absorption of light can be used as the
absorbing regions in black and white films. Prior to
development, the coat of a particle is a layer of silver
halide. During development, the silver halide is reduced to

30   a coat of silver that has the correct thickness for a plasmon

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resonance. Such nanoparticles require a relatively small

1   amount of silver to scatter and absorb light as efficiently
as do solid silver particles. These particles can be used to
decrease the amount of silver needed in photographic
emulsions, prints and films. For black and white

5   photography, a group of particles having plasmon resonances
at different frequencies should be combined in the emulsion.
An advantage of using such particles is that less silver is
required. Also, since a smaller particle can have a
significant absorption and a thinner layer of particles is

10   required, there can be some increase in the resolution of the
film.
          (3) Coated particles, which enhance the
frequency-dependent scattering and absorption (i.e. the
extinction), and hence transmit light that is colored, can be

15   used to decrease the amount of dyes needed in photographic
films and slides. For applications where the light is
transmitted through the emulsion, colored light can be
generated using either scattering or absorption or any
combination. The particles in a color photographic film or

20   slide that go into the layer whose transmitted light is to
appear red (for example), are particles that, when developed,
absorb and scatter blue and yellow light, while transmitting
the red. The particles, before development, have a layer of
silver halide that has a thickness such that, when developed,

25   the resulting thickness of the silver coat and the thickness
of the other layers result in a particle that absorbs and
scatters as desired. The advantage of using such particles
is that they will replace dyes which are expensive.
          (4) Coated nanoparticles having a plasmon resonant

30   light scattering spectrum can be used to decrease the amount

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of dyes needed in color prints since the light reflected from

1   these particles is colored. These particles should have a
relatively large plasmon enhancement of the frequency
dependent scattering and a relatively smaller enhancement of
the frequency dependent absorption. Relatively large

5   nanoparticles, typically having diameters in the range of 60
to 200 nanometers, should be used since their ratio of
scattering to absorption is larger. The particles, before
development, have a layer of silver halide that has a
thickness such that, when developed, the resulting thickness

10   of the silver coat and the thicknesses of the other layers
result in a particle that scatters as desired. The particles
in a photographic print placed in the layer of the emulsion
that is to appear red (for example), are particles that, when
developed scatter red light. Such particles can also be used

15   for color copiers and colored inks.

       (5) Coated nanoparticles having a plasmon resonant
enhancement of the absorption of light can be used to
decrease the amount of silver needed in the absorbing layers
of photographic emulsions, prints and films. These particles

20   should have a more enhanced absorption than scattering and
hence are particularly small, in the range 5 to 60
nanometers. Such particles can be used to replace the
Cary-Lea sols now used to absorb stray light in both black
and white and in color films. They can also be used as the

25   absorbing regions in black and white films. An advantage of
using such particles is that less silver is required.

       (6) Emulsions in which combinations of the above
particles and effects, and particles in which the above
advantages and effects are combined are also useful. An

30   example of a particle in which (1) and (2) is employed is a

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particle having a dielectric core, a silver coat, a polymer
coat and then a silver halide coat. The plasmon resonance
enhances the fields in the silver halide layer. When the
silver halide is developed to silver, the plasmon resonances
in the scattering and absorption by the particle provide the
5   advantages described in (2) above. The particles described
in (5) can also be used in the same emulsion.

To achieve the advantages described in (2), (3) and
(4) above, it is preferable that the silver halide coat is
reduced to a relatively smooth silver coat. With reference
10 to Figure 5A, one way to force the reduced silver to form a
smooth coat on the dielectric is to precoat the original
particles 16 with a polymer 16C that is porous enough to
allow ions to pass. For example, the coat 16C can prevent
Ag+ ions from migrating to sites on the surface next to the
15 polymer. The polymer 16C encourages the Ag+ to go to the
positions where growth is desired. Such a polymer coat can
be made in a manner similar to that specified herein.

Also, independently of the photographic process,
this is another way to make silver coated particles.
20   Figures 2-5 are only representative of
nanoparticles that may be used in the practice of the present
invention, and in particular, only illustrate the general
relationship between the cores and the shells of the shown
particles. In any nanoparticle used in this invention, the
25 particle and the core thereof may have any suitable shapes,
and specifically, the particles and the cores may have shapes
other than spherical. For instance, the particles and the
cores may be cylindrical or ellipsoidal, have a thread-like
shape, or be crystalline shaped. The actual crystal form of
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the core may be any suitable form; and, for example, these

1   cores may be:

Tetragonal crystal forms,

Orthorhombic crystal forms,

Monoclinic crystal forms,

5   Triclinic crystal forms,

Isometric crystal forms,

Hexagonal crystal forms.

Furthermore, the emulsion 10 may include a mixture of particles of different sizes and shapes, and the emulsion

10   may include silver halide particles of the type convention-ally used in photographic emulsions. Still further, any suitable dielectric material may be used in the particles employed in this invention; and, in particular, the dielectric material may be linear or non-linear. In

15   addition, as the term is used herein, "metal" includes any material having a negative dielectric constant, and so can include superconductors, conducting polymers, and materials with an anomalous dispersion of carrier electrons, and heavily doped semiconductors where free carrier motion

20   dominates the dielectric function.

The development of emulsion 10 is based, in part, on the fact that at various wavelengths of light, silver coated dielectric spheres may be made that absorb and scatter light at a much higher efficiency than do solid silver

25   spheres of the same size, and this fact is demonstrated in Figures 6-11.

Figures 6-11 show the light absorption efficiency of solid silver spheres and silver coated silica spheres at various wavelengths of light; and in particular, at

30   wavelengths of 355nm, 382nm, 414nm, 497nm, 621nm and 828nm

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respectively. The efficiencies were computed using a
procedure described by Toon and Ackerman, Applied Optics,
1981. The light absorption efficiency, Q, of the particles
is plotted along the vertical axis of each Figure; and a size
parameter, x, equal to $2\pi r/\lambda$, where r is the radius of the
particle and λ is the wavelength of interest for the
respective Figure, is plotted along the horizontal axis of
each Figure. Curves 32a, 34a, 36a, 40a, 42a, and 44a of
Figures 6-11 indicate the light absorption efficiencies of
solid silver spheres. Curves 32b-d, 34b-f, 36b-e, 40b-g,
42b-f and 44b-e indicate the light absorption efficiencies of
silver coated silica spheres; and in particular, each of
these curves represent a constant value (shown in
parenthesis) for the ratio of the diameter of the internal
silica core to the diameter of the whole coated sphere.

Thus, for instance, the values determined from
curve 32b of Figure 6 are for silver coated silica spheres
comprising an internal silica core having a diameter that is
half the diameter of the whole coated sphere, and the
absorption values determined from curve 36d of Figure 8 are
for silver coated silica spheres comprising an internal
silica core having a diameter that is 0.6 times the diameter
of the whole coated sphere.

For example, Figure 6 shows that at a wavelength of
355nm, for a coated sphere having an outside diameter of
about 113nm (x=1.0) and including an internal silica core
having a diameter half that of the whole coated sphere, the
absorption efficiency of that coated sphere is about 0.93.
Similarly, Figure 9 shows that at a wavelength of 497nm, for
a coated sphere having an outside diameter of about 79nm
(x=0.5) and including an internal silica core having a

1   diameter that is 0.7 times the diameter of the outside
diameter of the whole coated sphere, the absorption
efficiency of that coated sphere is about 5.2.

      Figures 10 and 11 show that, for spheres having
outside diameters between 1 and 100 nanometers and for light

5   in the wavelength range of 621 to 828 nanometers, spherical
particles comprised of silica cores coated with an
appropriate thickness of silver absorb many times more light
than do solid silver spheres of the same diameter. For
example, Figure 10 shows that at a wavelength of 621nm,

10   first, the absorption efficiency of a solid silver sphere
having an outside diameter of about 198 nanometers ($x= 1.0$)
is about 0.3, and second, a coated sphere having the same
outside diameter and an internal silica core having a
diameter 0.9 times the diameter of the whole coated sphere,

15   has an absorption efficiency of about 2.0, which is more than
six times the absorption efficiency of the solid silver
sphere of the same size. Figure 11 shows that at a
wavelength of 828nm, first, the absorption efficiency of a
solid silver sphere having an outside diameter of about 132

20   nanometers ($x= 0.5$) is about 0.2, and second, a coated sphere
having the same outside diameter and an internal silica core
having a diameter 0.9 times the diameter of the whole coated
sphere, has an absorption efficiency of about 5.8, which is
about twenty-nine times the absorption efficiency of the

25   solid silver sphere of the same size.

      Figures 6 and 7 show that, in the near ultraviolet
wavelengths (at wavelengths of 355 and 382 nanometers), the
solid silver spheres absorb more light than do the silver
coated silica cores, at least with spheres between 1 and 100

30   nanometers in diameter. However, with some of the larger

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spheres, some of the silver coated particles absorb as much

1   or more light in the ultraviolet wavelengths than do the
solid silver spheres. Also, with some of the larger sizes of
the spheres, the silver coated particles and the solid silver
spheres have similar absorption efficiencies. The absorption

5   cross section of a sphere is the absorption efficiency of
that sphere multiplied by πr^2, where r is the radius of the
sphere.

Similar wavelength dependent spectra are also
observed in the scattering and extinction spectra. With

10 smaller sized spheres, say 10 nm, the absorption is greater
than the scattering and with larger sized coated spheres, say
200 nm, the scattering can be greater than the absorption
when there is an appropriate thickness of core to coat.
Figures 11a and 11b show: (1)λ dependent spectra, and (2) $Q_s \ll Q_a$

15 when the particles are small. Figure 11c shows $Q_s \sim Q_a$ when
diameter $\sim$ 100nm. Figures 11d and 11e show C_{abs}/Vol for
coated sphere $\gg$ than for the solid sphere especially when
$\lambda > 500$ nm.

Because the light absorption profile of each coated

20 particle is a function of the diameter of the internal silica
core, the thickness of the coating on that core, and the
wavelength of the light incident on the particle, a desired
light absorption profile can be obtained for a film emulsion
by combining appropriate amounts of different sizes of coated

25 particles, which in certain instances might be in combination
with uncoated particles. To avoid repeating the phrase
"absorption, scattering or extinction profile" too many
times, in the following description of the synthesis of a
profile we refer to it only as an absorption profile although

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the method works just as well for scattering or extinction
1   spectra.

        One way to synthesize an absorption profile is to
take a multitude of coated particles that absorb light over a
wavelength range of interest, to separate that multitude of
5   particles into groups according to the sizes or coating
thicknesses of the particles, and then to form a mixture of
particles from these groups, with the amount or proportion of
particles taken from each group weighted so that the
resulting mixture has the desired absorption profile.
10   For instance, assume that a particular absorption
profile, $D(\lambda)$, is desired over the wavelength range of
visible light, and that the initial multitude of coated
particles absorbs light over this wavelength range, with
these particles being dispersed in water and with the
15   dielectric cores of the coated particles having uniform
diameters of approximately 30nm. The coated particles can be
grouped according to their coating thicknesses; and, for
example, the particles can be separated into 14 groups having
coating thicknesses of 1.5nm, 1.75nm, 2.0nm, 2.25nm, 2.5nm,
20   3.0nm, 3.5nm, 4.0nm, 4.5nm, 5.0nm, 6.0nm, 7.0nm, 9.0nm, and
12.0nm respectively. The light absorption of each group of
particles can be expressed as a function of the wavelength of
light incident on the particles; and, more generally, the
absorption of the ith group of particles can be expressed as
25   $A_i(\lambda)$, where λ is the wavelength of the light incident on the
particles.

        The actual absorption profile, $T(\lambda)$, of a mixture
containing N groups of particles can be expressed as follows:

30
$$T(\lambda) = \sum_{i=1}^{N} a_i A_i(\lambda)$$

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where a_i is the proportion of the ith group of particles in
the mixture. To achieve the desired absorption profile, the
a_i (that is a_1, $a_2 \ldots a_N$) are chosen so that $T(\lambda)$ is equal to
or closely approximates $D(\lambda)$. Any suitable procedure may be
used to determine or to estimate the a_i. According to one
very well known technique, the a_i can be estimated to
minimize the sum, or the integral, C, of the squares of the
difference between $D(\lambda)$ and $T(\lambda)$. According to this
technique,

$$C = \int (D(\lambda) - T(\lambda))^2 d\lambda$$

The set of a_i that minimizes this difference can be
found or suitably estimated by many known methods such as by
a gradient search procedure (for example, as disclosed in
"Practical Methods of Optimization," by Fletcher (1981)).
Numerous computer programs are also known and may be used to
estimate or determine the set of a_i that minimizes the
difference between $D(\lambda)$ and $T(\lambda)$.

The mixture of coated particles needed to achieve
the desired absorption profile is then made by combining the
N groups of particles, each weighted by the associated a_i.

Another way to obtain a film emulsion with a
desired light absorption profile is to form the film emulsion
from a series of layers, with the layers containing different
particle sizes or types.

Figures 12 and 13 illustrate two embodiments of a
second type of light sensitive recording medium, generally
referenced at 50a and 50b respectively, and also according to
the present invention. This medium is a light sensitive
optical recording disk or plate, comprising a solid, light
reflecting or light transmitting substrate 52 and a multitude

of particles 54 carried by that substrate. The particles 54

1   may be carried directly by substrate 52, as shown in Figure
12; or, as illustrated in Figure 13, the particles 54 may be
dispersed in a colloid or gel 56 that is applied onto the
substrate. Each of the particles 54 includes a core

5   surrounded by a shell, and at least one of the core and shell
consists essentially of a metal. Preferably, the other of
the core and shell consists essentially of a dielectric
material; and more specifically, preferably the core of each
of these particles consists essentially of a dielectric

10 material, and the shell of each particle consists of a metal.

To record data in medium 50a or 50b, a light beam,
referred to as a write beam, of sufficient intensity to
change the morphology of the coated particles 54, such as by
melting the silver coating or the dielectric core, is passed

15 over the recording medium in a given pattern to change the
morphology of the particles over a path or selected areas, to
thereby represent stored data. Because of this change in
morphology, the portions of the medium that were exposed to
the write beam are very much less able to absorb light than

20 are the portions of the medium that were not exposed to the
write beam.

Another light beam, referred to as a read beam, of
an intensity low enough so that it does not change the
morphology of the particles 54, can then be passed over the

25 recording medium. The read beam is reflected or transmitted
when it strikes a portion of the recording medium previously
exposed to the write beam, while the read beam is absorbed
when it strikes a portion of the recording medium not
previously exposed to the write beam. In this way, the read

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beam can be used to determine, or read, the data stored in
1   the recording medium.

        As will be appreciated by those of ordinary skill
in the art, in any nanoparticle used in this invention, the
particle and the core thereof may have any suitable shapes,
5   and specifically, the particles and the cores may be
cylindrical or ellipsoidal, have a thread-like shape, or be
crystalline shaped. Also, the write beam may be used to
change these particles in various specific ways to produce
the desired results. Moreover, with the particles 54 that
10 include dielectric material, any suitable dielectric material
may be used, and in particular, that dielectric may be a
linear or a non-linear material. In addition, as the term is
used herein, "metal" includes any material having a negative
dielectric constant, and so can include superconductors,
15 conducting polymers, materials with an anomalous dispersion
of carrier electrons, and heavily doped semiconductors where
free motion dominates the dielectric function.

        The following considerations are helpful in forming
and selecting suitable or preferred particles for use in the
20 recording media illustrated in Figures 12 and 13.

        i)   at light wavelengths at which the plasmon
resonance effect shown by certain particles is significant
(referred to as resonance frequencies), the electromagnetic
fields around the particles are enhanced,

25   ii)   the electromagnetic fields, or the heat caused
by the absorption of those fields, in and around certain
particles can cause those particles to change so that they
absorb or scatter less light,

        iii)   the plasmon resonance effect exhibited by
30 small metal-dielectric layered particles is dependent on the

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size and dielectric constants of those layers, and particles
1   can be made so that only a comparatively small change in the
physical structures of the particles results in significant
changes in the way in which, or the extent to which, the
particles absorb or scatter light, and
5   iv) magnetic materials become non magnetic when
heated to or above the Curie points of the materials.
            Based on the above facts, particles 54 for
recording media 50a and 50b can be made so that, on the one
hand, a write beam can be used to change significantly the
10   ability of the particles to absorb or scatter light, but on
the other hand, the ability of the particles to absorb or
scatter light will not change significantly in the absence of
the write beam.
            For example, with a first general class of
15   particles, the particle may comprise a core and first and
second layers of materials over that core, with each of these
layers comprised of a material different than the material of
the other layer, and the write beam may cause these two
materials to react with each other to form a third material
20   having a dielectric constant different than the dielectric
constants of the original materials of the particles. Figure
14 shows a particle 60 comprising core 60a, first layer 60b
and second layer 60c, and one of these layers 60b and 60c is
a dielectric, such as an oxide, and the other of these layers
25   60b and 60c is a metal, such as silver. The energy of the
write beam may cause layers 60b and 60c to react with each
other to form a dielectric, silver oxide. The altered
particle is shown at 62 in Figure 15, and this particle
consists of core 62a and the formed dielectric layer 62b.
30   Because the formed particle 62 does not have a layer of

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metal, that particle does not exhibit the plasmon resonance
1   effect; and, consequently, the light absorption and
reflection characteristics of particle 62 are significantly
different than the light absorption and reflection
characteristics, respectively, of particle 60.

5   As another example, Figure 16 shows a particle 64
comprised of a core 64a and first and second layers 64b and
64c, and each of these latter two layers is comprised of a
respective one type of dielectric material. The write beam
may cause these dielectric materials to react with each other
10 to form a third dielectric material having a dielectric
constant different than the dielectric constants of the
materials used to form layers 64b and 64c. This altered
particle is shown at 66 in Figure 17, and the particle
consists of core 66a and the formed dielectric material 66b.

15   With a second general class of particles,
represented by particle 70 of Figure 18, the particle
includes a core 70a and one or more outside layers 70b and
70c, with one of these layers being comprised of a monomer.
The write beam causes the monomer layer to polymerize,
20 changing that layer to a solid that has a dielectric constant
different than the dielectric constant of the monomer. The
formed particle is shown at 72 in Figure 19; and the particle
comprises core 72a, first layer 72b and polymer layer 72c.
To make particle 70 itself, it may be preferred to form or
25 apply the layer of monomer 70c onto the core 70a of the
particle at low temperatures.

            With a third general class of particles, the write
beam is used to change the shape of the particle and thereby
change its light absorption or reflection characteristics.
30 For example, Figure 20 shows a non-spherical particle 74

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comprised of a core 74a and first and second shells 74b and
74c. The energy from the write beam that is absorbed by the
particle 74 causes shell 74c to melt, and then the surface
tension between the remaining shell 74b and the medium in
which the particle is suspended, causes the shell and the
core to become spherical. The formed particle is shown at 76
in Figure 21, and the particle comprises core 76a and shell
76b. The plasmon resonance effect exhibited by particle 76 is
different than the plasmon resonance effect exhibited by
particle 74, and thus the light absorption and light
reflection characteristics of the former particle are
different than those of the latter particle.

With a fourth general class of particles, the write
beam is used to melt the outside layer of the particle, and
this melted material then mixes with and changes the
dielectric constant of the medium surrounding the particle or
of the substrate on which the particle is carried. For
instance, Figure 22 shows particle 80 comprising core 80a and
shells 80b and 80c, dispersed in a medium 82. In use, the
write beam melts shell 80c, and the material from the shell
mixes with medium 82. The result of this process is
illustrated in Figure 23, which shows particle 84, comprising
core 84a and shell 84b, dispersed in a medium 86. The
plasmon resonance effect exhibited by particle 84 in medium
86 is different than the plasmon resonance effect shown by
particle 80 in medium 82. As a result, the light absorption
and reflection characteristics of particle 84 in medium 86
are different, respectively, than the light absorption and
reflection characteristics of particle 80 in medium 82.

With a fifth class of particles, the write beam is
used to melt the outside layer of the particle and to change

the structure of an inner layer of the particle, for example,
1 from amorphous to crystalline or from crystalline to
amorphous. Figure 24 shows a particle 90 of this type, and
comprising core 90a and shells 90b and 90c. The write beam
melts outside shell 90c and changes the structure of inside
5 shell 90b, producing a particle shown at 92 in Figure 25,
comprising core 92a and shell 92b. The plasmon resonance
effect produced by particle 92 is different than that shown
by particle 90, and consequently, the light absorption and
reflection characteristics of these two particles differ.

10 A sixth class of particles includes a layer of a
magnetized material, and the energy of the write beam is used
to raise the temperature of this material above the curie
point of that material, where it is no longer magnetic. For
example, Figure 26 shows a particle 94 of this general type,
15 and including core 94a comprised of a magnetic material, and
shell 94b comprised of a metal. In operation, the write beam
raises the temperature of particle 94 to a level above the
curie point of core 94a, so that the core is no longer
magnetic. As another example, Figure 27 shows a particle 96
20 that includes core 96a and two shells 96b and 96c. Core 96a
consists of a dielectric material, shell 96b is a metal, and
shell 96c is a magnetic material. In recording media 50a or
50b, a write beam is used to raise the temperature of shell
96c to a point above its curie point so that the shell ceases
25 to be magnetic.

As will be understood by those of ordinary skill in
the art, reversible procedures may be used to alter the
particles of recording media 50a and 50b, producing a
write-many read-many system. For example, the coated spheres
30 could be used to enhance the fields only to increase the

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temperature to the curie point (as low as 150°C for some

1   magnetic materials used in optical discs) and a magnetic field can be used to set the orientation of the magnetic domains. This procedure could be reversible.

The above-discussed changes, and other similar

5   changes, produced by a write beam will alter the extent to which light is absorbed by or transmitted through a recording medium. The particles in recording media 50a or 50b may be either located on a surface, such as in an optical disk, or dispersed throughout a volume. When the particles are

10 dispersed throughout a volume, it may be preferred to provide that volume with a low density of such particles. In addition, layered particles in which a metal is reacted with a dielectric to form another dielectric, such as particle 60, may be particularly useful for forming volume phase

15 holograms. Particles in which the polymerization of a monomer is initiated by the write beam may also be particularly useful for forming volume phase holograms.

Sensitizers used with conventional photographic emulsions may be used with the coated spheres employed in the

20 photographic emulsion of the present invention, either on the outside of or on the inside of the silver halide layer.

Also, the silver-halide emulsion of this invention may be treated by many known chemical sensitization methods. For example, the emulsion may be treated by a sulfur

25 sensitization method using a sulfur-containing compound capable of reacting with active gelatin and silver (e.g., a thiosulfate, a thiourea, a mercapto compound or a rhodamine); a reduction sensitization method using a reducing material (e.g., a stannous salt, an amine, a hydrazine derivative,

30 formamidinesulfinic acid or a silane compound); or a noble

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metal sensitization method using a noble metal compound

1 (e.g. a gold complex salt, complex salts of metals belonging to group VIII of the periodic table, such as Pt, Ir or Pd).

As a protective colloid for use in the preparation of the silver halide emulsions of this invention, gelatin may

5 be used but other hydrophilic colloids may be used, such as, for example, gelatin derivatives; graft polymers of gelatin and other polymers; proteins such as albumin and casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose and cellulose sulfuric acid esters;

10 sugar derivatives such as sodium alginate and starch derivatives; and various synthetic hydrophilic polymers or copolymers such as polyvinyl alcohol, partial acetal of polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole and

15 polyvinyl pyrazole.

As gelatin, lime-processed gelatin as well as acid-processed gelatin, and enzyme-processed gelatin may be used, as well as the hydrolyzed products and enzyme-decomposition products of gelatin.

20 Various compounds can be added to the silver halide photographic emulsions of this invention for stabilizing the photographic properties of the emulsions and for preventing the formation of fog during the production, storage, or processing of the photographic materials containing the

25 silver halide emulsions. Examples of antifoggants and stabilizers include benzothiazolium salts; nitroimidazoles; nitrobenzimidazoles; cholorbenzimidazoles; bromobenzimidazoles, mercaptothiazoles; mercaptothiadiazoles; aminotraizoles; benzotraizoles; nitrobenzotriazoles;

30 mercaptotetrazoles; mercaptopyrimidines; mercaptotriazines;

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1   thioketo compounds such as oxazolinethione; azaindenes such as triazaindenes, tetraazaindenes, pentaazaindens; benzenethio-sulfonic acid; benzenesulfinic acid; and benzenesulfonic acid amide.

5   The silver halide photographic emulsions of this invention may further contain polyalkylene oxides or the derivatives thereof, such as the ethers, esters, amines, thioether compounds; thiomorpholines; quaternary ammonium salt compounds; urethane derivatives; urea derivatives; imidazole derivatives; and 3-phyrazolidone derivatives for

10 increasing sensitivity and contrast or for accelerating the development of the photographic materials containing the silver halide emulsions.

        The silver halide photographic emulsions of this invention may be spectrally sensitized by methine dyes,

15 including cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyannine dyes, styrl dyes, and hemioxonol dyes. Particularly useful dyes are cyanine dyes, merocyanine dyes, and complex merocyanine dyes. For these dyes, conventional

20 cyanine dye nuclei such as basic heterocyclic nuclei can be used, including a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a tetrazole nucleus and a pyridine nucleus. The foregoing nuclei may be fused to aromatic hydrocarbon rings, such as an

25 indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a napththoxazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus.

        A 5- or 6-membered heterocyclic nucleus having a

30 ketomethylene structure such as a pyrazoline-5-one nucleus, a

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1 thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, rhodanine nucleus or thiobarbituric acid nucleus can be used as a nucleus for the merocyanine dyes or complex merocyanine dyes.

These sensitizing dyes may be used alone or in 5 combination, and a combination of sensitizing dyes is frequently used for supersensitization.

The silver halide photographic emulsions of this invention may further contain dyes having a spectral sensitizing action or materials which do not substantially 10 absorb visible light but which exhibit a supersensitizing effect when used together with the foregoing sensitizing dyes.

The photographic materials using the silver halide emulsions of this invention may contain water-soluble dyes as 15 filter dyes or for various purposes such as irradiation prevention. Examples of such dyes are oxonal dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Among these dyes, oxonol dyes, hemioxonol dyes and merocyanine dyes are useful.

20 The photographic materials containing the silver halide emulsions of this invention may contain stilbene series, triazine series, oxazole series, or cumarine series whitening agents in the silver halide emulsion layers and other hydrophilic colloid layers. These materials may be 25 water soluble or water insoluble and in the latter case, they may be used as dispersions.

Known fading preventing agents may be used along with color image stabilizers in this invention, alone or in combination. The photographic materials using the silver 30 halide emulsions of this invention may further contain

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hydroquinone derivatives, aminophenol derivatives, gallic

1 acid derivatives and ascorbic acid derivatives, as color fogging preventing agents.

The silver halide photographic emulsions of this invention can be used for both black and white photographic

5 materials and multilayer multicolor photographic materials. A multilayer natural color photographic material ordinarily has at least one red-sensitive layer, at least one green-sensitive layer and at least one blue-sensitive silver halide emulsion layer on a support. The red-sensitive layer

10 usually contains a cyan dye-forming coupler, the green-sensitive layer contains a magenta dye-forming coupler, and the blue-sensitive layer contains a yellow dye-forming coupler, but if desired, other combinations may be employed.

As the yellow coloring couplers, known closed chain

15 ketomethylenic couplers can be used, including benzoylacetoanilide series compound and pivaloylacetoanilide series compounds. As magenta coloring couplers, pyrazolone series compounds, indazolone series compounds and cyanoacetyl compounds can be used and pyrazolone series compounds are

20 particularly useful. As cyan coloring couplers, phenolic compounds and naphtholic compounds and couplers having a ureido group can be used. DIR couplers (development inhibitor releasing couplers) can also be used in this invention.

25 The photographic materials using the silver halide emulsions of this invention may contain compounds capable of releasing development inhibitors (apart from DIR couplers) with the progress of the development. Also, couplers capable of releasing development accelerators or fogging agents with

30 the process of development can be used in this invention.

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The photographic materials containing the silver

1   halide emulsions of this invention may contain ultraviolet
absorbents in the hydrophilic colloid layers, such as aryl
group-substituted benzotriazole compounds. 4-thiazolidone
compounds; benzophenone compounds, cinnamic acid ester

5.   compounds, butadiene compounds and benzoxydol compounds. In
addition, ultraviolet absorbents can be used in this
invention. Still further, ultraviolet absorbing couplers
(e.g., a-naphtholic cyan dye-forming couplers) and
ultraviolet absorbing polymers may be used in this invention.

10   These ultraviolet absorbents may be mordanted in specific
layers of the photographic materials.

For processing the photographic materials
containing the silver halide emulsions of this invention,
known processes and known processing solutions can be used.

15   The processing temperatures are usually in the range of about
18°C. to 50°C. but may be lower than 18° C. or higher than
50°C. According to the purposes, a development processing
forming silver image (black and white development process) or
color photographic process composed of development process

20   for forming dye images can be used for developing the
photographic materials.

The color developer which is used for developing
the photographic materials of this invention is generally
composed of an alkaline aqueous solution containing a color

25   developing agent. Color developing agents include aromatic
primary amino color developing agents such as
phenylenendiamines (e.g., 4-amino-N,N-diethylaniline,
3-methyl-4-amino-N,N-diethylaniline,
4-amino-N-ethyl-N-B-hydroxyethylaniline,

30   3-methyl-4-amino-N-ethyl-N-B-hydroxyethylaniline,

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3-methyl-4-amino-N-ethyl-N-B-methanesulfoamide-ethylaniline

1   and 4-amino-3-methyl-N-ethyl-N-B-methoxyethlaniline).

The photographic emulsion layers are usually
bleached after color development. The bleach process may be
performed simultaneously with or separately from the fix

5   process. Bleaching agents include compounds of multivalent
metals such as iron(III), cobalt(III), chromium(VI) and
copper(II); peracids; quinones and nitroso compounds such as
ferricyanides; dichromates; organic complex salts of
iron(III) or cobalt(III); aminopolycarboxylic acids such as

10   ethylenediaminetetraacetic acid, nitrotriacetic acid and
1,3-diamino-2-propanoltetraacetic acid; complex salts of
organic acids such as citric acid, tartaric acid and malic
acid; persulfates; permanganates and nitrosophenol. Among
these materials, potassium ferricyanide,

15   ethylenediaminetetraacetic acid iron(III) sodium salt and
ethylenediaminetetraacetic acid iron(III) ammonium salt are
particularly useful. The ethylenediaminetetraacetic acid
iron(III) complex salts are useful for a bleach solution and
for a fix solution.

20   Any suitable procedure may be used to prepare the
coated particles used in the recording media of the present
invention. For example, with reference to Figure 28, silver
halide coated dielectric particles, such as particle 16 of
Figure 2, may be made by a process generally comprising the

25   steps of providing an aqueous solution including negatively
charged colloidal dielectric particles, positively charged
silver ions, and a halide, and reacting the halogen of the
halide with the silver ions to bond, or grow, coatings of
silver halide completely covering individual dielectric

30   particles. Preferably, the concentrations of dielectric

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may be dispersed in the solution, then the silver ions may be
1   added, and then the halide may be added.

With a preferred process, after the dielectric
particles are added to the solution, the pH of that solution
is adjusted to and thereafter maintained at a level slightly
5   above 2, and even more preferably, between about 3 and 5.
With this procedure, the dielectric particles do not have to
be negatively charged when they are added to the solution,
and, instead, the acidity of the aqueous solution causes the
dielectric particles to become negatively charged once the
10   particles are in the solution. Further, with the preferred
process, the initial concentration of the silver ions in the
solution is relatively low, less than 10^{-4}M; the initial
concentration of the halide in the solution is slightly
greater than, such as about 10% greater than, the
15   concentration of the silver ions in the solution; and also,
the solution is constantly stirred while the halide is being
added to it.

The silver ions may be added to the solution in any
suitable form, and for instance, these ions may be added in
20   the form of a soluble salt, e.g., silver nitrate. Likewise,
the halide that is added to the solution may be any suitable
halide, such as an alkali halide, e.g., sodium bromide,
sodium chloride, potassium bromide, potassium bromide and the
like. In addition, any suitable dielectric may be used in
25   the above-discussed process, and the dielectric may be linear
or non-linear and may have any suitable shape and size. For
example, the dielectric particles may be spherically shaped
silica particles. When, first, the dielectric particles are
these silica particles, second, the silver ions are added to
30   the solution in the form of silver nitrate, and third, the

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halide is sodium bromide, then the silver from the silver

1   nitrate reacts with the bromide from the sodium bromide to
form silver bromide, which bonds to and forms layers over the
silica particles.

          Figure 29 generally outlines a process for making a
5   metal coating on a dielectric particle, such as coating 20b
of particle 20, or coating 22b of particle 22. This process
generally comprises the steps of providing an aqueous
solution including negatively charged colloidal dielectric
particles, metal ions, a secondary alcohol containing 3-7
10 carbon atoms, and an alkyl ketone containing 3-7 carbon
atoms; removing oxygen from the solution; and exposing the
solution to ultraviolet light to cause the metal ions to
attach to the dielectric particles and form metal coatings
completely covering individual dielectric particles.
15 Preferably, the concentrations of the dielectric particles,
the metal ions, the isopropanol and the acetone, and the
length of time the solution is exposed to the ultraviolet
light are selected so that coatings of a uniform, preselected
thickness are formed on the dielectric particles.

20   As used herein, the term lower alkyl, when used
alone or in combination, contain 1-7 carbon atoms. These
alkyl groups may be staight chained or branched and include
such groups as methyl, ethyl, propyl, isopropyl, butyl,
sec-butyl, isobutyl, t-butyl, pentyl, amyl, hexyl, heptyl,
25 and the like. As used herein, a secondary alkanol refers to
a lower alkyl alcohol in which the hydroxy group is attached
to a secondary carbon. Such groups include isopropanol,
sec-butanol and the like.

          The preferred alkyl ketone is acetone.
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In the above-discussed procedure, without wishing
to be bound, it is believed that the ketone (acetone) absorbs
energy from the ultraviolet light and then reacts with the
secondary alcohol (isopropanol) to form alkyl secondary
(isopropyl) radicals. These radicals are powerful reducing
agents and cause metal ions that have become attached to the
dielectric particles to form metal molecules. The particular
order in which the dielectric particles, the metal ions, the
secondary alcohol and the ketone are added to the aqueous
solution is not critical; and, for instance, the secondary
alcohol and ketone may be added to the solution, the
dielectric particles may then be dispersed in the solution,
and then the metal ions may be added.

With a preferred process, as with the process
outlined in Figure 28, after the dielectric particles are
added to the solution, the pH of the solution is adjusted to
and thereafter maintained at a level slightly above 2, and
even more preferably, between about 3 and 5. In this way,
the dielectric particles do not have to be negatively charged
when they are added to the solution and the acidity of the
aqueous solution causes the dielectric particles to become
negatively charged. In addition, the initial concentration
of the metal ions in the solution is relatively low, such as
$2 \times 10^{-4}M$; and the initial concentration of the acetone and
isopropanol in the solution are about equal to each other and
much greater than, such as about 400 times greater than, the
initial concentration of the metal ion in the solution. In
addition, preferably the solution is stirred while exposed to
the ultraviolet light.

Numerous specific types of metal coatings may be
made using a procedure as described above. The types of

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metals that can be used include transition metals, the
lanthanides and the Group IIIA metals. The especially
preferred metals include the Group VIII and IB metals,
especially copper, silver, gold, iron, nickel, palladium,
platinum, cobalt, rhodium, iridium, ruthenium, aluminum and
the like. Especially preferred metals include copper,
silver, gold, nickel, palladium, platinum and nickel.

It is most preferred that the process may be used
to form silver coated dielectric particles, gold coated
particles or palladium coated particles. In addition, the
metal ions may be provided in the solution in any suitable
manner; and, for example, these ions may be provided by
adding a water soluble metal salt such as silver nitrate, to
the solution.

Moreover, any suitable dielectric may be used in
the above-discussed process, and the dielectric may be linear
or non-linear and may have any suitable shape and size. For
instance, the dielectric particles may be spherically shaped
silica particles. When such dielectric particles are used,
and the metal ions are added to the solution in the form of
silver nitrate, then the ultraviolet light, in combination
with the acetone and the isopropanol, causes the silver ions
to bond to and form metal silver coatings over the silica
particles.

1   EXAMPLE 1

             The following example illustrates this process for
      forming metal coated dielectric particles.
5   An aqueous solution is prepared by mixing the
      following solutions in a 50 ml beaker:
             (1) 0.5 ml of 0.01 M $AgNO_3$,
             (2) 0.5 ml of 0.50 M of low porosity SiO_2
      particles.
10   The particle diameter is chosen to be between 5 to 20
      nanometers, although other sizes can be readily substituted,
             (3) 1.5 ml of pure isopropanol,
             (4) 1.5 ml of pure acetone.
             All chemicals used are of reagent grade quality,
15   unless otherwise specified. The above mixture is diluted
      with 16 ml of distilled water, and the pH adjusted to be
      between 4 to 5 by dropwise addition of a 0.01 M nitric acid
      solution. In this pH range, the silica particles are
      negatively charged, causing the positively charged silver
20   ions to be bound to the surface. After thorough mixing by
      stirring for one minute using a magnetic stirrer, the sample
      is transferred to a UV photolysis vessel, equipped with a
      quartz window and provision for careful deoxygenation by
      bubbling nitrogen gas for one hour. It is important that no
25   oxygen be present in the solution. The sample is irradiated
      by a 450 Watt Hg-Xe lamp for one hour, with gentle stirring
      continued by means of a magnetic stirrer. The solution
      color, and consequently the thickness of the coat, can be
      controlled by adjusting the period of illumination by UV
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light. This forms the basis for the preparation of the

1   silver coated silica particles in the present example.

      Silver coated dielectric particles may also be made
by a process employing photoreduction of silver halide, and
one such process is outlined in Figure 30. In this process,

5   silver halide coated dielectric particles are made, for
example, by the process discussed above in connection with
Figure 28, and then the coated particles are exposed to light
to change the silver halide coatings over the individual
particles to metal silver coatings.

10   Preferably, though, a more integrated process,
generally outlined in Figure 31, is used to form silver
coated dielectric particles. In accordance with this
process, dielectric particles are dispersed in a solution
including silver ions, a halide and an electron hole

15   scavanger, and the silver ions react with the halogen of the
halide to form silver halide coatings completely covering the
dielectric particles. The solution is then exposed to
ultraviolet light, and this light changes the silver halide
coatings to silver coatings. Preferably, the concentrations

20   of the dielectric particles, the silver ions, the halide and
the electron hole scavanger in the solution, and the length
of time the solution is exposed to the ultraviolet light are
selected so that coatings of a uniform, preselected thickness
are formed on the dielectric particles.

25   Preferably, with this process, the initial
concentration of silver ions in the solution is greater than
the initial concentration of the halide in the solution; and
for instance, the former concentration may be about 5 times
the latter concentration. The silver ions may be in the

30   solution in any suitable form, and for instance, these ions

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may be added to the solution in the form of a salt that is

1   soluble in aqueous solution, e.g., silver nitrate.
Similarly, the halide that is added to the solution may be
any suitable halide such as an alkali halide, e.g., sodium
bromide, sodium chloride, potassium bromide, potassium

5   chloride, and the like. Further, any suitable dielectric may
be used in this process, and the dielectric may be linear or
non-linear and have any suitable shape and size. For
example, the dielectric particles may be spherically shaped
silica particles. When (i) the dielectric particles are the

10   silica particles, (ii) the silver ions are added to the
solution in the form of silver nitrate, and (iii) the halide
is sodium bromide, then the silver from the silver nitrate
reacts with the bromide from the sodium bromide to form
silver bromide; and the ultraviolet light, in the presence of

15   EDTA, then reduces the silver bromide coatings to metallic
silver.

        In the above procedure, it is preferred that the
light source used contain ultraviolet light. It is preferred
that the light source contain wavelength ranging from 150-550

20   nm. The preferred wavelengths range from 200-400 nm.

        Furthermore, it is preferred that the intensity of
light used ranges from 50 watts to 1.5 kilowatts, with the
preferred intensity ranging from 250-1000 watts. Especially
preferred intensity ranges from 350-550 watts, with an

25   intensity of about 450 watts being the most preferred.

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EXAMPLE 2

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      Metallic silver on SiO_2 particles can be obtained
by photoreduction of silver halides, which are typically
prepared in the presence of excess Ag^+ ions. A hole (h^+)

5   scavanger, EDTA, is added to the solution. One ml of a 0.002
M NaBr solution is added to 19 ml of a solution which is
prepared in a 50 ml beaker by mixing the following:

(1) 1 ml of 0.01 M $AgNo_3$,

(2) 0.5 ml of 0.50 M of low porosity SiO_2 particles. The

10   particle diameter was 12 nanometers, although other sizes can
be readily substituted,

(3) 1 ml of 0.02 M EDTA,

(4) 16 ml of distilled water.

      After thorough mixing, the solution is transferred

15   to a 1 cm UV quartz cuvette and exposed to a 375 Watt
tungsten halogen light source. Under these conditions, very
little light is actually absorbed since the colloidal AgBr
has a very low absorbance above 350 nm. A possible mechanism
for the reduction process is given by:

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$$AgBr \longrightarrow AgBr(e^- + h^+)$$
$$AgBr + e^- \longrightarrow Ag^o + Br^-$$
$$EDTA + h^+ \longrightarrow product$$
$$Br^- + Ag^+(excess) \longrightarrow AgBr$$
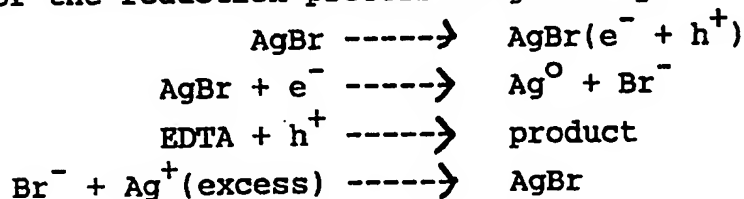
      The duration of illumination, which is in the order

25   of minutes, determines the color of the silver coated silica
particles. This color is a result of the thickness of the
silver layer, and can range from yellow to a purplish gray.

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Once the silver coated silica spheres are prepared,
1 they are purified by dialysis and then placed in a sodium
dodecyl sulfate micellar solution, or a microemulsion.

A variation of the process described above may be
employed to form metal coatings other than silver on nano
5 particles, and this variation utilizes the fact that metallic
silver on the dielectric particles will act as a catalyst to
help grow metal coatings on those particles from other metal
ions in the solution. In accordance with this variation,
which is outlined in Figure 32, a solution is provided
10 including dielectric particles, silver halide is formed on
those particles, the solution is exposed to light to change
at least a portion of the silver halide to metallic silver,
and ions of a metal are added to the solution to form
coatings of that metal completely covering individual
15 dielectric particles, with the metallic silver on those
particles acting as a catalyst to accelerate the formation of
the metal coatings. These metal ions may be added to the
solution in any suitable manner, and for instance,
conventional photographic developing solutions may be added
20 to the solution to reduce the metal ions.

Only minute amounts of metallic silver are needed
on the dielectric particles to help grow the metal coatings
thereon; and hence, in the above-described process, it is
only necessary to form minute amounts of silver halide on the
25 dielectric particles. Alternatively, complete coatings of
silver halide may be formed on the dielectric particles, with
only minute amounts of the silver halide on individual

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particles being changed to metallic silver. With another
1 variation, silver halide coatings may be made completely
covering dielectric particles, only minute amounts of the
silver halide may be changed to metallic silver on individual
particles, and then these minute amounts of metallic silver
5 may be used to help form metal coatings completely covering
the silver halide that remains on the dielectric particles.
The resulting product comprises a dielectric core, a first
coating of silver that substantially completely covers the
dielectric core, and a second coating of a metal that
10 completely covers the layer of silver halide.

The following example illustrates the coating of
silver on a dielectric core of silver bromide. The silver
bromide nanoparticles exposed briefly to intense UV light in
the presence of EDTA have optical extinction spectra similar
15 to those computed for distribution of silver-coated silver
bromide nanoparticles. By intense, it is meant that the
intensity of the light ranges from 50 watts to 1.5 kilowatts,
with the preferred range being 250-550 watts, and the most
preferred having a range of 350-550 watts.
20   As clearly shown by the following discussion, with
shorter exposure time, the plasmon resonance maximum is
shifted to longer wavelengths, a result consistent with
theory so long as the coat thickness increases with exposure
to light. The resonance maximum of the distributions of
25 coated particles can be controllably shifted to 600 to 700
nm.

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EXAMPLE 3

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  Silver bromide colloids were prepared by rapidly
mixing equal volumes of $AgNO_3$ and NaBr solutions. A growth
stabilizer (SDS) and an electron doner (EDTA) were added

5 immediately after precipitation. Typically the final
concentrations were 1×10^{-4} M Br^-, 4×10^{-4} mAg^+, 5×10^{-4} M
(SDS). and 5×10^{-4} M EDTA. The concentration of SDS was far
below the critical micellization concentration (10^{-2} M).
Freshly prepared solutions were exposed to light from a 450

10 Watt Hg-Xe lamp for a few seconds. With the shortest
exposures the spectra appeared blue. With longer exposures
the solution appeared orange. When ammonia, which dissolves
AgBr by forming complexes with Ag^+ was added to any of the
illuminated solutions the color changed to a yellow color

15 characteristic of small metallic silver colloids.
  The particle size distributions were characterized
with transmission electron microscopy (JEOL 1200EX). A
typical micrograph is shown in (Fig. 19a). A size
distribution consistent with the limited micrograph data is

20 the log normal distribution.

$$N(r)=N_o \exp(-((\ln(r)-\ln(r_m))/\ln(s))^2), \qquad (1)$$

with r_m equal to 1 nm or less and s in the range of 4 to 4.5

25 nm. The size distributions as determined by TEM did not
appear to change markedly with exposure to light.
  After the addition of ammonia to any of the
illuminated samples only small particles having diameters 5
nm or less were observed in the TEM (Fig 19b). The most

30 likely interpretation is that only part of the AgBr was

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reduced to Ag during the illumination and that the larger

1   particles are AgBr/Ag composites.

Example optical extinction spectra measured shortly
after exposure are shown in Figs 20a) to d). The exposure
time and/or EDTA concentration and hence the reduction of

5   Ag^+, increases in going from a) to d). The peak extinction
shifts to shorter wavelengths as the illumination time is
increased. This result is consistent with theory so long as
the coat thickness increases with exposure. A spectrum of
the ammonia treated solution shown in Fig 20e), is typical of

10   homogeneous silver nanoparticles. The general shapes of the
above spectra are readily reproducible. At comparable
illumination times, in the absence of Br^-, the appearance of
color in a given sample is negligible.

Theoretical optical extinction spectra of

15   individual silver coated spheres are shown in Fig. 21. The
peak of the theoretical extinction shifts from red to blue as
the ratio of coat thickness to core radius increases. This
data is consistent with the measured spectra where the
absorption maxima shift toward the blue as the time of

20   exposure increases since the coat thickness should increase
with exposure time. The compound spectra are very sensitive
to the coat thickness. The measured spectra are much more
broad than the spectra shown in Fig. 21 because of the
distributions of core diameters and coat thicknesses.

25   The magnitudes of the extinction spectra are also
characteristic of silver coated particles. For example, at a
wavelength of 700 nm the extinction cross section per unit
volume of silver is 100's of times larger in a silver coated
nanoparticle having the appropriate ratio of core radius to

30   coat thickness than it is in a solid silver sphere. The fact

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that the theoretical extinction is so large can be used to

1   help verify that the particles are coated with silver.
However, since there is a broad distribution of sizes care
must be taken in making the comparison.

Here we started with the size disbribution of core

5   particles described by the above equation, then used trial
and error to determine the distributions of coat thicknesses
required to match the measured spectra, and then found that
the magnitudes of the spectra were within the range of values
expected from the initial concentrations of Ag^+ and Br^-.

10   The assumptions made in computing the spectra are
as follows:

1. The reduced silver is in the form of a smooth
coat on the surface of a spherical AgBr particle. The
extinction efficiencies were computed using the separation of

15   variables solution for concentric spheres based on
algorithms.

2. The size distribution of the core particles is
described by the log-normal distribution of the above
equation. The values of N_0 were determined by setting the

20   total volume of all the particles prior to illumination in
the distribution equal to the volume of AgBr. The initial
total volume of AgBr was determined by solving the ionic
equilibria equations including the Ag^+ - EDTA complex.

3. The size distribution of the coat thicknesses

25   is a Gaussian, typically with a standard deviation of 2 to 8
nm.

4. The silver coat may be formed either from the
reduction of the silver halide of the initial particle, or
from the reduction of Ag^+ from solution. Computations have

30   been done for each of the two limiting cases.

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5. The total extinction is computed by numerically
integrating over distributions of core radii and coat
thicknesses.

$$b_e(\lambda) = \quad N_n(r_c)N_g(t)Q(r_c,t,m_c,m_t,\lambda)\pi r^2 dr_c dt \quad (2)$$

where N_n is the size distribution of the cores, N_g is the
size distribution of the coats. Q is the extinction
efficiency, m_c is the refractive index of the core, and m_t is
the refractive index of the coat. Typically the integrations
over cores were from r = 2 to r = 18.

6. The refractive index fo the silver was computed
from the data of Hagemann et al. in J. OP. Soc. Am., 65,
742-744 (1975) and Kerker, in J. OP. Soc. Am. B., 1327-1329
(1985), either by itself, or combined with a Drude model in
which the increased electron scattering at the surfaces of
the very thin coat was taken into account. The refractive
index data of Johnson and Christy in Phy Rev. B, 6, 4370-4379
(1972) was also used for some computations not shown. Linear
interpolation was used to obtain the values of refractive
index at points not in the data.

7. The refactive index of AgBr was obtained by
combining the data from White, J. opt. Soc. Am., 62, 212
(1972), and James, "Theory of the Photographic Process",
MaMillan (1977) p. 216.

Fig. 41 shows a measured spectrum and two computed
spectra. In the topmost curve the Ag in the coat is assumed
to come only from the solution. i.e., the AgBr cores are not
reduced in size as the coat grows. In the bottom curve the
Ag in the coat is assumed to come only from the reduction of
AgBr at the surface of the particle and so the core shrinks

as the coat grows. Since the measured curve lies between the

1 two computed spectra, the magnitudes of the plasmon enhanced
extinction is in the range of values computed.

The main parameters that can be adjusted in fitting
the distributions to the spectra are: 1) the thickness and

5 standard deviation of the coats and the limits of the
numerical integration for the coats. 2) the size
distribution and limits of integration for the cores. 3) the
data for the refractive index of silver, the fraction of the
reduced silver that came from solution. The computed spectra

10 are very sensitive to the distributions of cores and coats
chosen and to the limits of integration, which also define
the size distributions. The computed spectra depend on the
refractive index of silver used. However, by varying the
size distributions, similar spectra can be obtained with the

15 different models for silver. The effect of the different
assumptions about the source of the Ag for the coat can be
seen in Fig. 40. In a preliminary experiment without excess
silver a spectrum similar to that shown in Fig. 39d was
generated.

20 Without wishing to be bound, it is believed that
the silver coat is formed by the coalescing of many small
silver particles. The coat may also contain some AgBr or
voids, but it is homogeneous enough to have a refractive
index similar to that of bulk silver. The bonds between the

25 particles may be relatively weak because the coat breaks into
many small particles when the solution is treated with
ammonia.

It might have been thought that the spectra could
be accounted for by nonsherical silver particles. The fact

30 that ammonia, which dissolves AgBr but not Ag, reduces the

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spectrum to that of small solid particles, and the fact that the particles in the TEM do not have large eccentricities, argue against this hypotheses. Also, the particle shapes do not seem to be related to the colors of the solutions.

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In summary, the predicted tunability of the surface-plasmon resonance frequency and enhanced extinction at longer wavelengths was experimentaly confirmed with Ag-AgBr colloidal composites. The particles scatter as if the Ag is smoothly coated on the AgBr.

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Silver coated dielectric particles may also be formed by a process utilizing chemical reduction of silver ions by hydroquinone at elevated temperatures. The following example, generally outlined in Figure 33, illustrates this process.

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EXAMPLE 4

1   100 ml of a silica solution (particle diameter 7
nm) which had been purified by overnight dialysis was
transferred to a 250 ml beaker, and the pH adjusted to 4.0 by
dropwise addition of 0.01 M $AgNO_3$ solution added dropwise
5 under gentle stirring to achieve the final concentration
shown in the table below. After about 2 minutes, sufficient
quantity of 0.01 M hydroquinone was added in a similar
manner. The reduction to metallic silver takes place
gradually over a time period of about five minutes,
10 accompanied by a color change from pale yellow to dark brown.
The rate of silver deposition by this method can be
controlled by varying the temperature between 85 to 95°C. A
transparent solution is obtained in every case, and is
allowed to cool and then purified by dialysis.

15   EXAMPLE 5

    The following table summarizes the experimental
conditions, including final concentrations (in molar), which
were used in four different sets:

	I	II	III	IV
SiO_2	1%	1%	1%	1%
$AgNO_3$	5.0×10^{-4}	1.0×10^{-3}	1.5×10^{-3}	2.0×10^{-3}
Hydro-quinone	5.0×10^{-5}	1.0×10^{-4}	1.5×10^{-4}	2.0×10^{-4}

25   The amount of silver deposited increases from I to
IV, and is evident from the color of the solutions (light
yellow to dark brown). Electron microscopy also provided
evidential support. The optical absorption specra show the
presence of a single peak maximum at about 400 nm.

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ELECTRON MICROSCOPIC RESULTS:

1   Solution I consists of particles which are smaller and better defined, appear darker, and were in the size range of 10 to 30 nm. In solution II, III, and IV, the particle size range was found to be between 40 to 100 nm, the

5 particles were similarly dark, but contained elongated as well as spherical shapes. The final size distribution may be due in part to the non uniform size of the silica core particles, found to be between 7 to 11 nm by electron microscopy.

10   With all of the processes described above, after the coated particles are prepared, they may be removed from the solution in which they were prepared by dialysis, and then placed in a sodium dodecyl sulfate micellar solution or a micro emulsion. Additional coatings of either silver

15 halide, a metal or a polymer, may then be added until the desired final configuration is reached. Polymer coating of any of these particles may be readily achieved in a solution by the well known emulsion polymerization method, in which a suitable amount of monomer and initiator have been added.

20   For instance, the following process, outlined in Figure 34, shows how a polymer coating may be made on a silver coated particle.

       The following aqueous stock solutions were prepared:

25   (I)   0.1 M KH_2PO_4,

   (II)   0.1 M NaOH,

   (III)   2 % solution of sodium salt of styrene sulfonic acid, NaSS (co-monomar),

   (IV)   3 % solution of $K_2S_2O_8$

30   All solutions were prepared in doubly distilled water, and all chemicals were reagent grade.

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1   131.6 ml of a 1% solution of the silver coated
       silica particles were transferred to a three necked flask. 8
       ml of solution IV, followed by 6.4 ml of solution II, were
       added with constant stirring using a magnetic stirrer. The
       flask was equipped with a condenser, and a platinum
5   thermometer, which, in combination with a thermoregulator and
       a heating mantle, allowed regulation of the temperature of
       the flask to 65 ± 1 °C. At this temperature, nitrogen gas
       was bubbled through the mixture continuously, and 30 ml of
       styrene was added. After 15 minutes, 10 ml of solution III
10   were added, and after another 20 minutes 4 ml of the
       initiator, solution IV, were added. Depending upon the
       thickness of the polymer film desired, the reaction can be
       terminated by addition of 25 ml of a 1 % solution of
       hydroquinone, and cooling the reaction mixture to room
15   temperature. The particles are filtered, washed several
       times with doubly distilled water, resuspended in water, and
       further purified by dialysis.

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1   EXAMPLE 6

            Coating of carbon fibres with copper was carried
    out by photochemical reduction of Cu^{++} using highly reductive
5   short lived 1-hydroxy-1-methylethyl radicals. These radicals
    were produced in situ by illuminating a mixture of 1 M
    acetone and 1 M propanol-2 with an UV source of Hg-Xe lamp
    operated at 450 watt. The reaction can be presented by

10                  $$(CH_3)_2CO \rightarrow (CH_3)_2CO^*$$

           $$(CH_3)_2CO^* + (CH_3)_2CHOH \rightarrow 2(CH_3)_2COH$$

        $$2(CH_3)_2COH + Cu^{+2} \rightarrow 2(CH_3)_2CO + Cu + 2H^+$$

15
                        $$nCu \rightarrow Cu_n$$
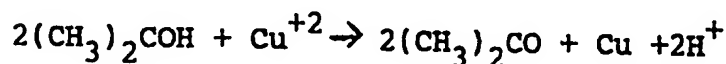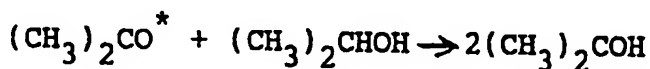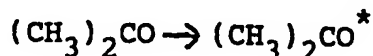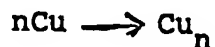
    Two different solutions of Cu^{++} (1×10^{-2} M and 1×10^{-3} M)
    were used to achieve two different coating thicknesses. Both
    solutions contained 1 M acetone, 1 M propanol-2, and carbon
20 fibers. The illumination time was two hours.
            These coated fibres, washed with distilled water
    and observed under an optical microscope, show a very fine
    and smooth coating and visibly exhibit a metallic lustre of
25 copper. The amount of copper on these fibres was detected
    using atomic absorption spectroscopy after removing the coat
    with 1 M nitric acid. The presence of copper on these fibres
    was also confirmed using Energy Dispersive Spectroscopy
    (EDS), which shows a peak for copper. The thickness of the
30 coat can be controlled by the copper concentration in

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solution and the duration of illumination. It can be readily

1   varied in the range of tens of nanometers to microns.

The processes discussed above may be used in
various combinations to form particles of a desired
configuration. For example, Figure 35 generally outlines a

5   procedure to make particle 20 of Figure 3. First, metal
coating 20b is formed over dielectric core 20a, for example
using the method illustrated in Figure 31; and then silver
halide coating 20c is made over metal layer 20b, for instance
by generally following the method shown in Figure 28.

10   Similarly, Figure 36 generally illustrates a procedure to
make particle 22 of Figure 4. In this procedure, first,
metal coating 22b is formed over dielectric core 22a, for
example by the process described above in connection with
Figure 29, then polymer coating 22c is applied over coating

15   22b, and then silver halide layer 22d is formed over coating
22c, for example by generally following the procedure
discussed above in connection with Figure 28.

While it is apparent that the invention herein
disclosed is well calculated to fulfill the objects

20   previously stated, it will be appreciated that numerous
modifications and embodiments may be devised by those skilled
in the art, and it is intended that the appended claims cover
all such modifications and embodiments as fall within the
true spirit and scope of the present invention.

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CLAIMS

1   1. A light sensitive silver halide photographic emulsion, comprising:

         a colloid; and

         a multitude of silver halide particles dispersed in
5   said colloid, each of said particles including a core surrounded by a shell, one of said core and shell consisting essentially of silver halide, and the other of the core and shell consisting essentially of a dielectric material.

         2. A photographic emulsion according to claim 1,
10   wherein said dielectric material is substantially free of silver atoms.

         3. A photographic emulsion according to claim 1, wherein each of the particles further includes a layer of a metal disposed between the core and the shell of the
15   particle.

         4. A photographic emulsion according to claim 3, wherein each of the particles further includes a layer of polymeric material disposed between the layer of the metal and said one of the core and shell of the particle.
20   5. A photographic emulsion according to claim 1, wherein:

         the core of each particle consists essentially of dielectric material; and

         the shell of each particle consists essentially of
25   silver halide.

         6. A photographic emulsion according to claim 5, wherein each of the particles further includes a layer of a metal disposed between the core and the shell of the particle.

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7.   A photographic emulsion according to claim 6,
wherein each of the particles further includes a layer of
polymeric material disposed between the layer of metal and
the shell of the particle.

8.   A photographic emulsion according to claim 7,
wherein:

the layer of metal of each particle substantially
completely covers the core of the particle; and

the layer of polymeric material of each particle
substantially completely covers the layer of metal of the
particle.

9.   A photographic emulsion according to claim 1,
wherein each of the particles further includes a polymer
coating extending around the shell of the particle.

10.   A photographic emulsion according to claim 2,
wherein each of the particles further includes a polymer
coating extending around the shell of the particle.

11.   A photographic emulsion according to claim 5,
wherein each of the particles further includes a polymer
coating extending around the shell of the particle.

12.   A light sensitive silver halide photographic
emulsion, comprising:

a colloid; and

a multitude of silver halide particles, each of
said particles consisting of

i)   a core consisting essentially of a dielectric
material,

ii)   a first shell consisting essentially of a
metal, and disposed immediately over and substantially
completely covering the core of the particle;

          iii)   a second shell consisting essentially of a

1   polymeric material, and disposed immediately over and

substantially completely covering the first shell of the

particle, and

          iv)   a third shell consisting essentially of a

5   silver halide, and disposed immediately over and

substantially completely covering the second shell of the

particle.

          13.   A photographic emulsion according to claim 12,

wherein the dielectric material of the core is substantially

10   free of silver.

          14.   A photographic emulsion according to claim 13,

wherein the first shell of each particle consists essentially

of silver.

          15.   A photographic emulsion according to claim 9,

15   wherein the core of each particle consists of silica.

          16.   The use of the enhanced plasmon resonance

effect to increase absorption and scattering processes.

          17.   A light-sensitive recording medium,

comprising:

20   a solid, light reflecting or light transmitting

substrate;

          a colloid applied onto the substrate; and

          a multitude of particles dispersed in said colloid,

each of the particles including a core surrounded by a shell,

25   at least one of the core and shell consisting essentially of

a metal.

          18.   A recording medium according to claim 17,

wherein the other of the core and shell consists essentially

of a dielectric material.

30

19. A recording medium according to claim 18,

1 wherein:

the core of each particle consists essentially of the dielectric material;

the shell of each particle consists essentially of

5 the metal; and

each of the particles further includes a layer of polymeric material disposed over and substantially completely covering the shell of the particle.

20. A light sensitive optical recording medium,

10 comprising:

a support medium;

a multitude of particles supported by the support medium, each of the particles including a core and a shell, one of the core and shell consisting essentially of a metal.

15 21. A recording medium according to claim 20, wherein the other of the core and shell consists essentially of a dielectric material.

22. A recording medium according to claim 21, wherein each of the particles further includes another shell

20 consisting essentially of silver halide.

23. A light sensitive recording medium, comprising:

a solid, light reflecting or light transmitting substrate;

25 a colloid applied onto the substrate; and

a multitude of particles dispersed in the colloid, each of the particles consisting of

i) a core consisting essentially of a dielectric material,

30

35

ii)   a shell disposed immediately over and
substantially covering the core, and consisting of a metal,
and

iii)   a coating disposed immediately over and
substantially covering the shell, and consisting essentially
of a polymeric material.

24.   A recording medium according to claim 23,
wherein the shell of each particle consists of silver.

25.   A method of storing and reading data in an
optical recording medium of the type having a solid, light
reflecting or light transmitting substrate and a multitude of
particles carried by the substrate, the method comprising the
steps of:

passing a write beam over the recording medium in a
given pattern to change the morphology of said particles over
a selected area of the recording medium to represent stored
data therein; and

passing a read beam over the recording medium to
read data stored therein;

wherein said particles are nanoparticles, each
nanoparticle including a plurality of layers, the plurality
of layers including a core surrounded by a shell, one of said
core and said shell consisting essentially of a metal.

26.   A method according to Claim 25, wherein:

one layer of each nanoparticle comprises a first
material having a first dielectric constant, and another
layer of each nanoparticle comprises a second material having
a second dielectric constant; and

the step of passing the write beam over the
recording medium includes the step of using the write beam to
react the first and second materials, of each of a multitude

of nanoparticles, with each other to form a third material
having a third dielectric constant different than the first
and second dielectric constants.

27. A method according to Claim 25, wherein:

one layer of each nanoparticle is a monomer; and

the step of passing the write beam over the
recording medium includes the step of using the write beam to
polymerize the monomer layer of each of a multitude of
nanoparticles over the selected area.

28. A method according to Claim 25, wherein the
step of passing the write beam over the recording medium
includes the step of using the write beam to change the shape
of each of a multitude of nanoparticles over the selected
area.

29. A method according to Claim 25, wherein:

the nanoparticles are suspended in a medium having
a dielectric constant; and

the step of passing the write beam over the
recording medium includes the step of using the change in
morphology in said particles to change the dielectric
constant of the medium over the selected area.

30. A method according to Claim 25, wherein the
step of passing the write beam over the recording medium
includes the step of using the write beam to melt one layer
and to change the shape of another layer of each of a
multitude of nanoparticles over the selected area.

31. A method according to Claim 25, wherein the
step of passi g the write beam over the recording medium
includes the step of using the write beam to melt one layer
and to change the structure of another layer of each of a
multitude of nanoparticles over the selected area.

32. A method according to Claim 25, wherein:

a layer of each of the nanoparticles is comprised of a magnetized material; and

the step of passing the write beam over the recording medium includes the step of using the write beam to de-magnetize the magnetized material of a multitude of nanoparticles over the selected area.

33. A method according to claim 25, wherein:

a layer of each of the nanoparticles is comprised of a magnetized material; and

the step of passing the write beam over the recording medium includes the step of using the write beam to heat the magnetic region either of the particle, or surrounding the particle, to its curie temperature while that region of the medium is subjected to an externally applied magnetic field so that the magnetic domains become oriented along the direction of the field.
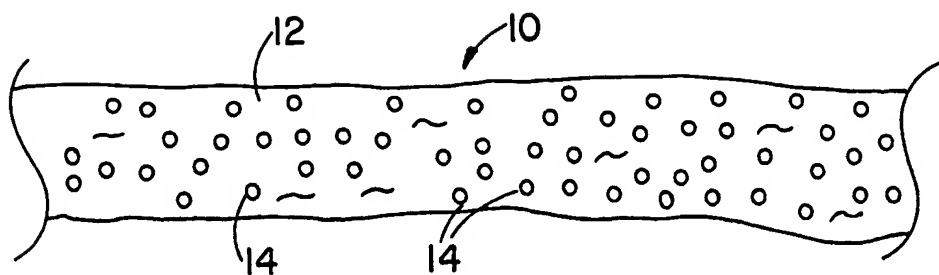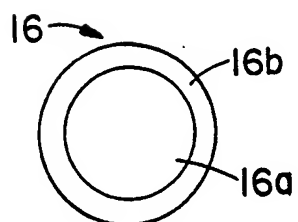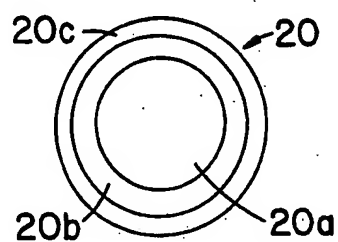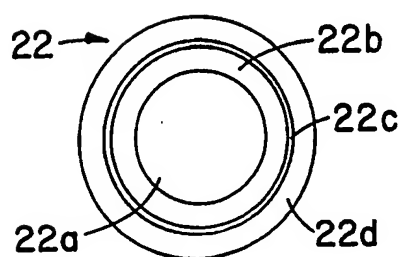
FIG.1

FIG.2

FIG.3

FIG.4
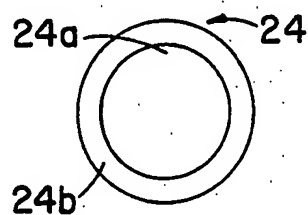
FIG.5
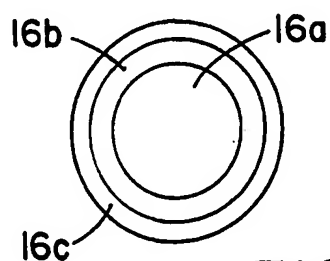
FIG.5a
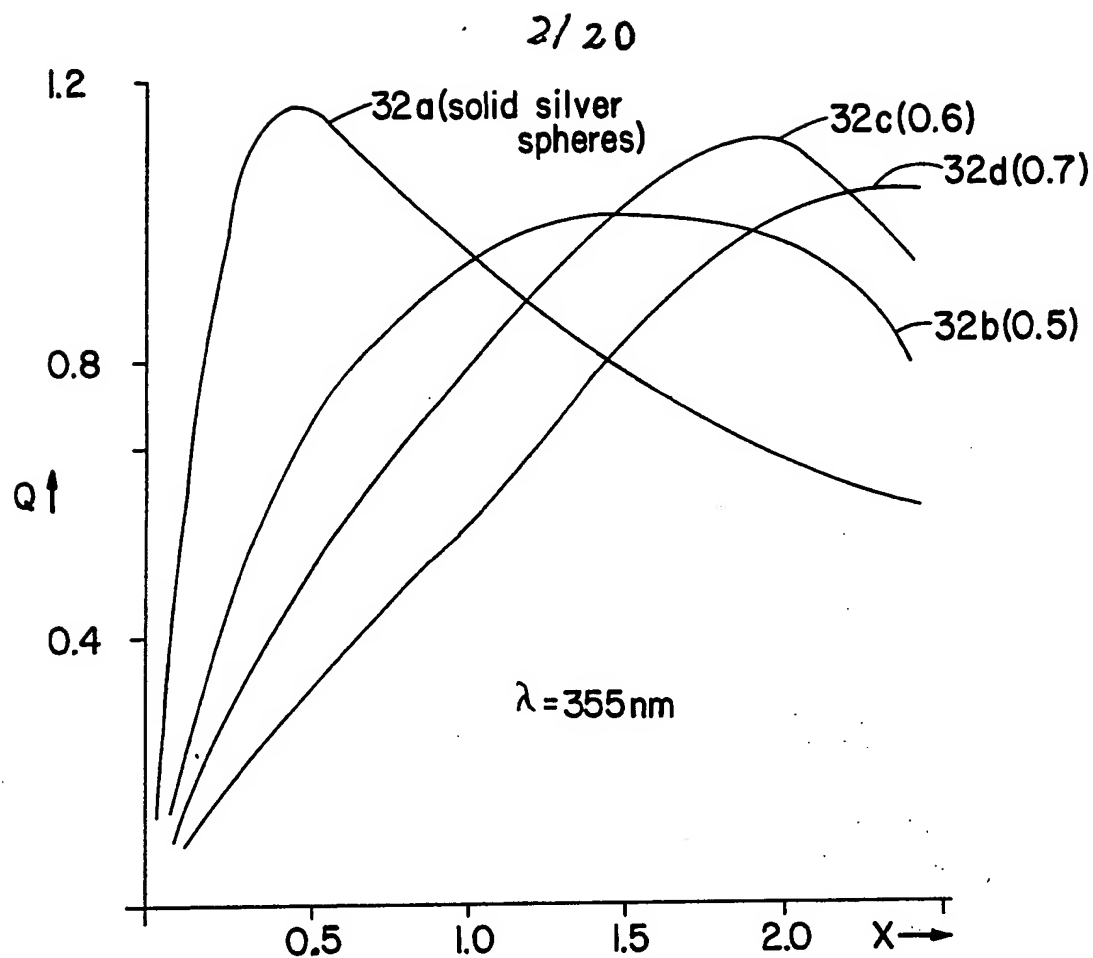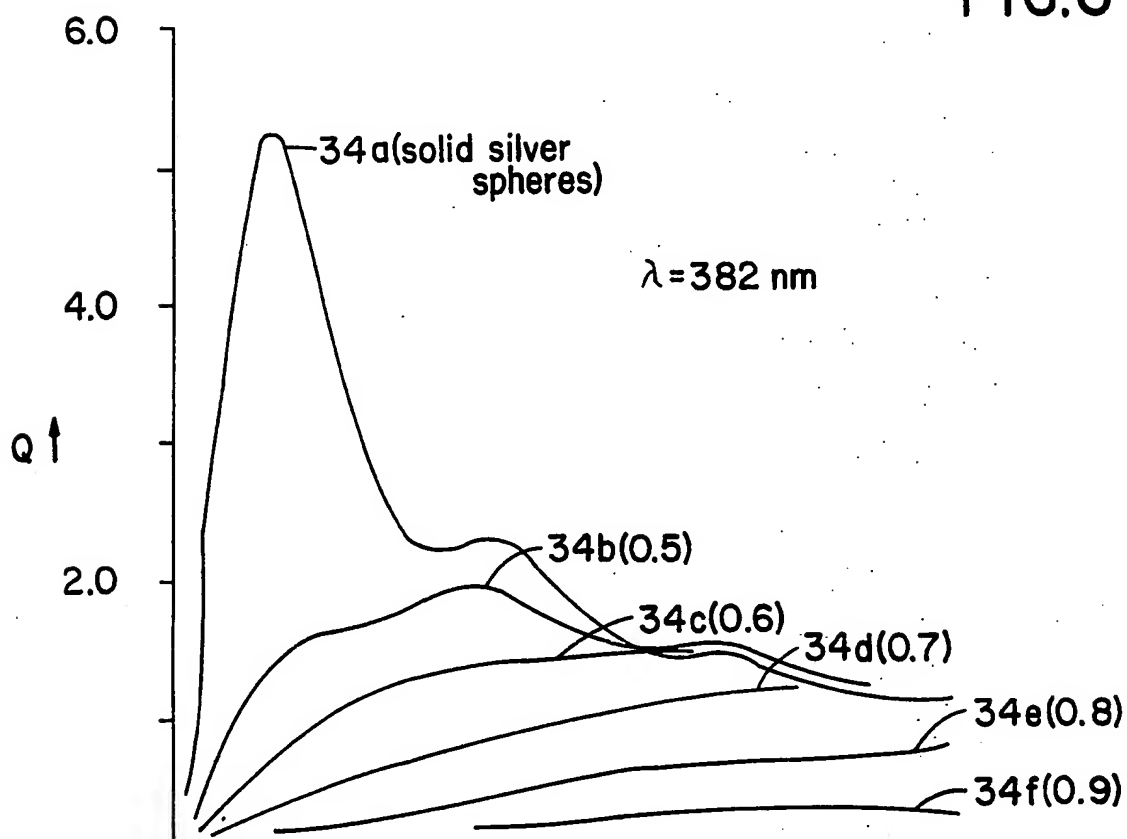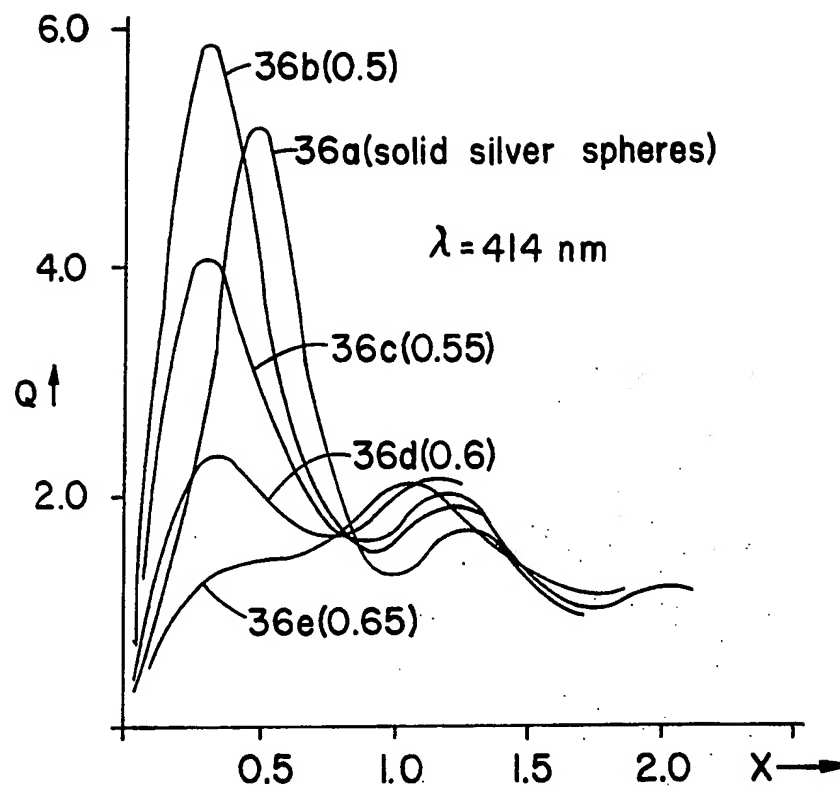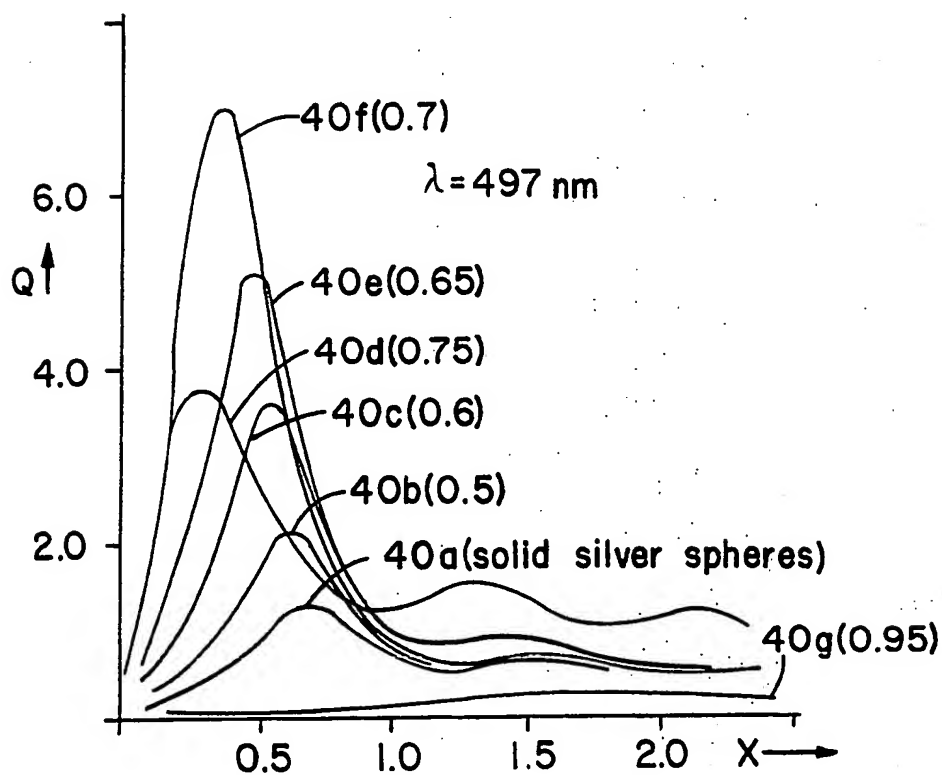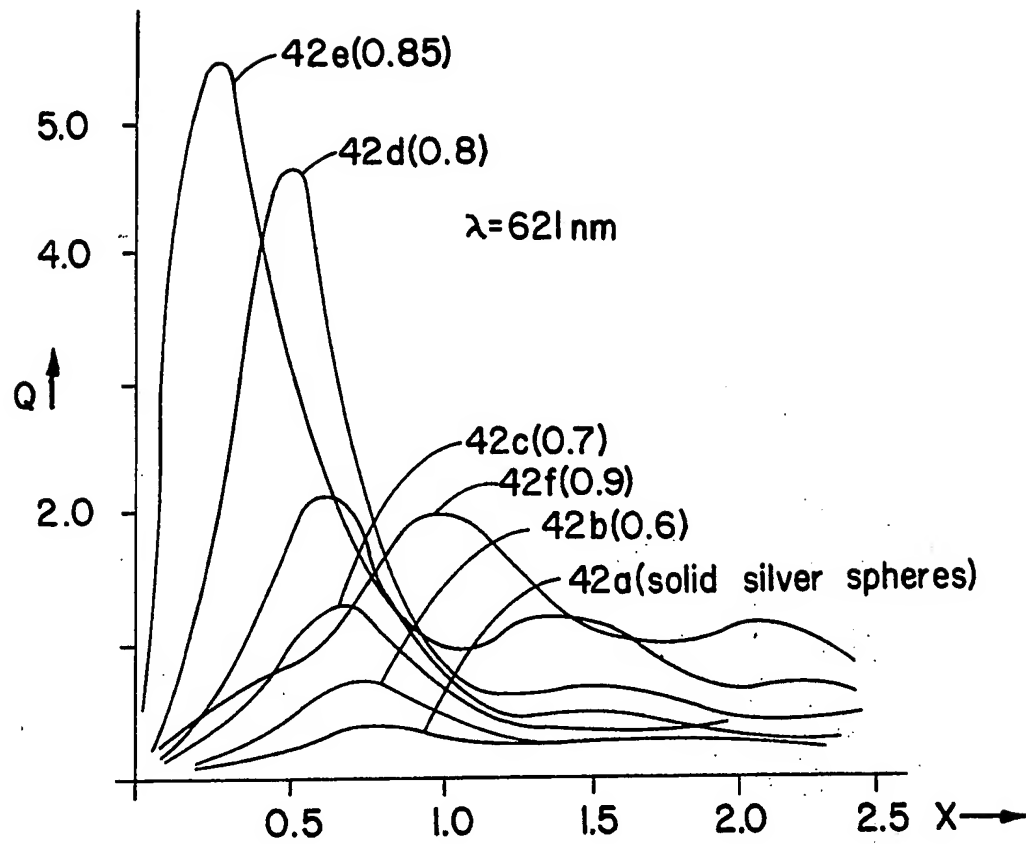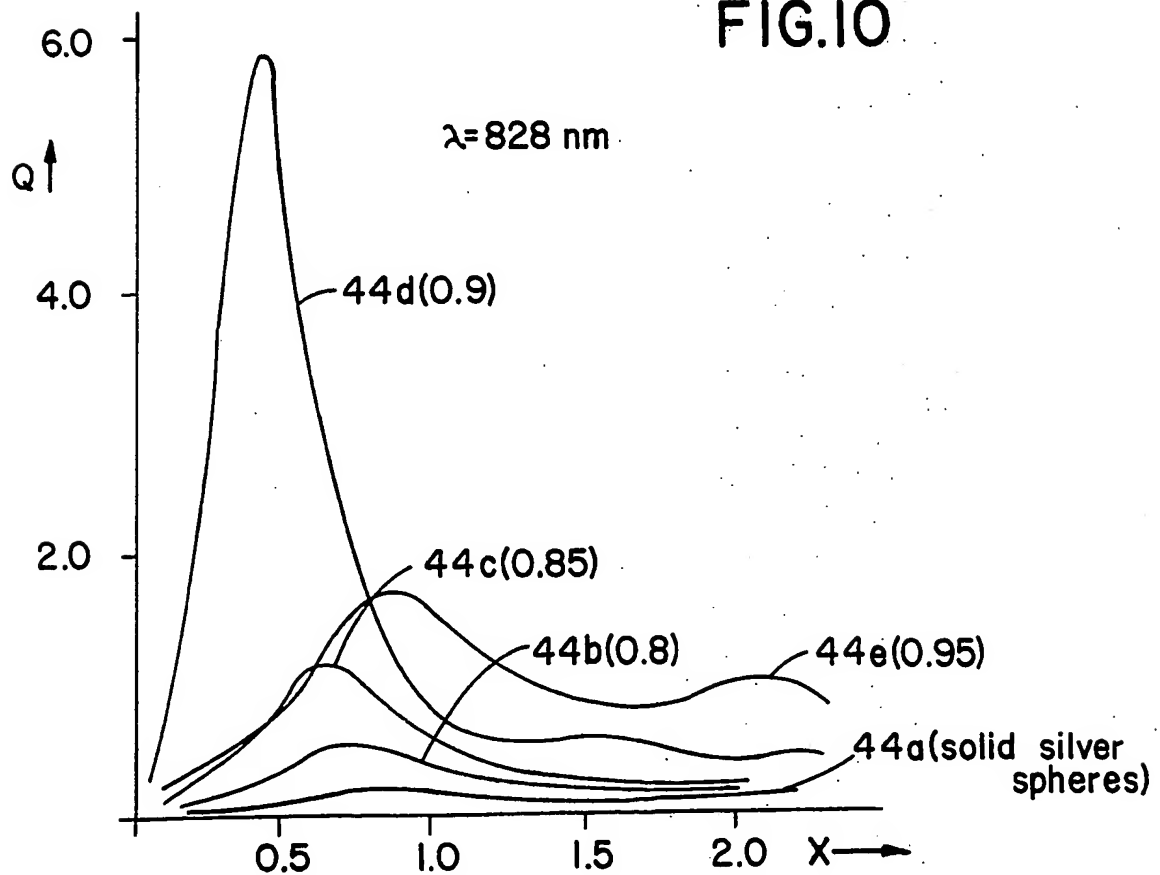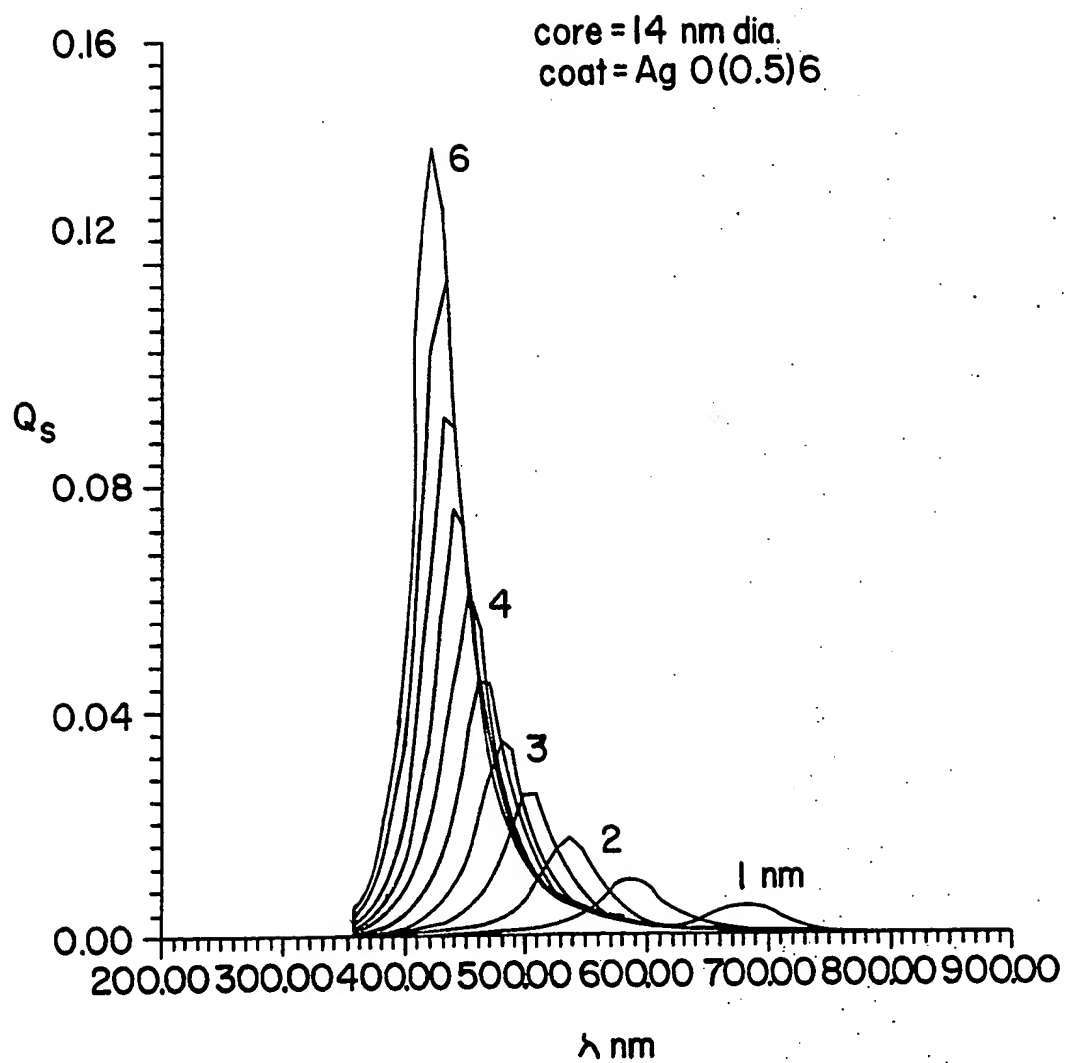
2/20

FIG.6

FIG.7

FIG.8

FIG.9

FIG.10
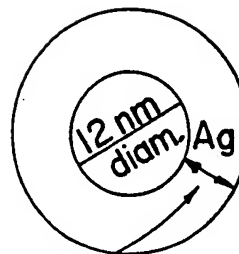
FIG.11
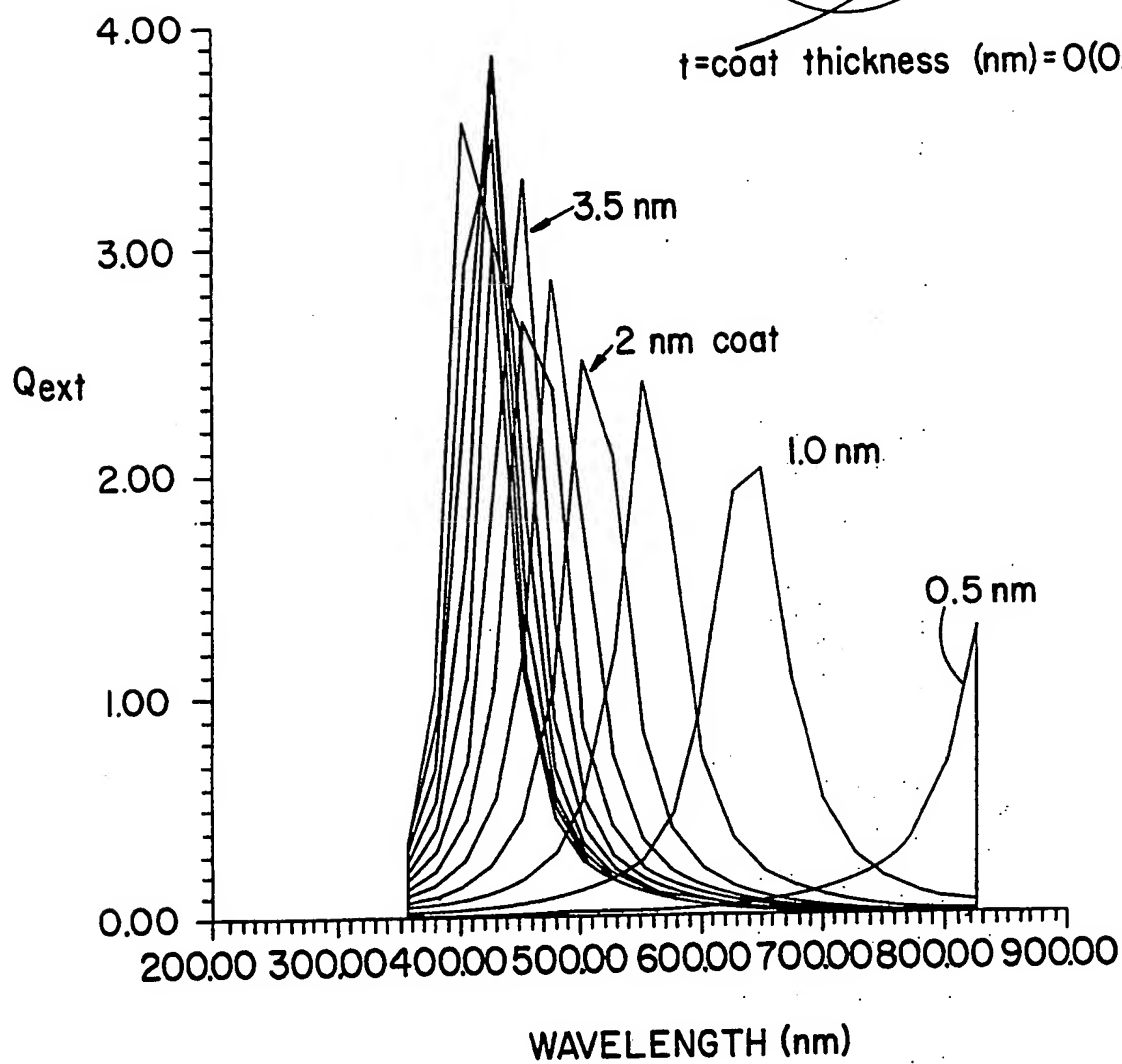
FIG.IIa

FIG. IIb

FIG.IIc

FIG.IId
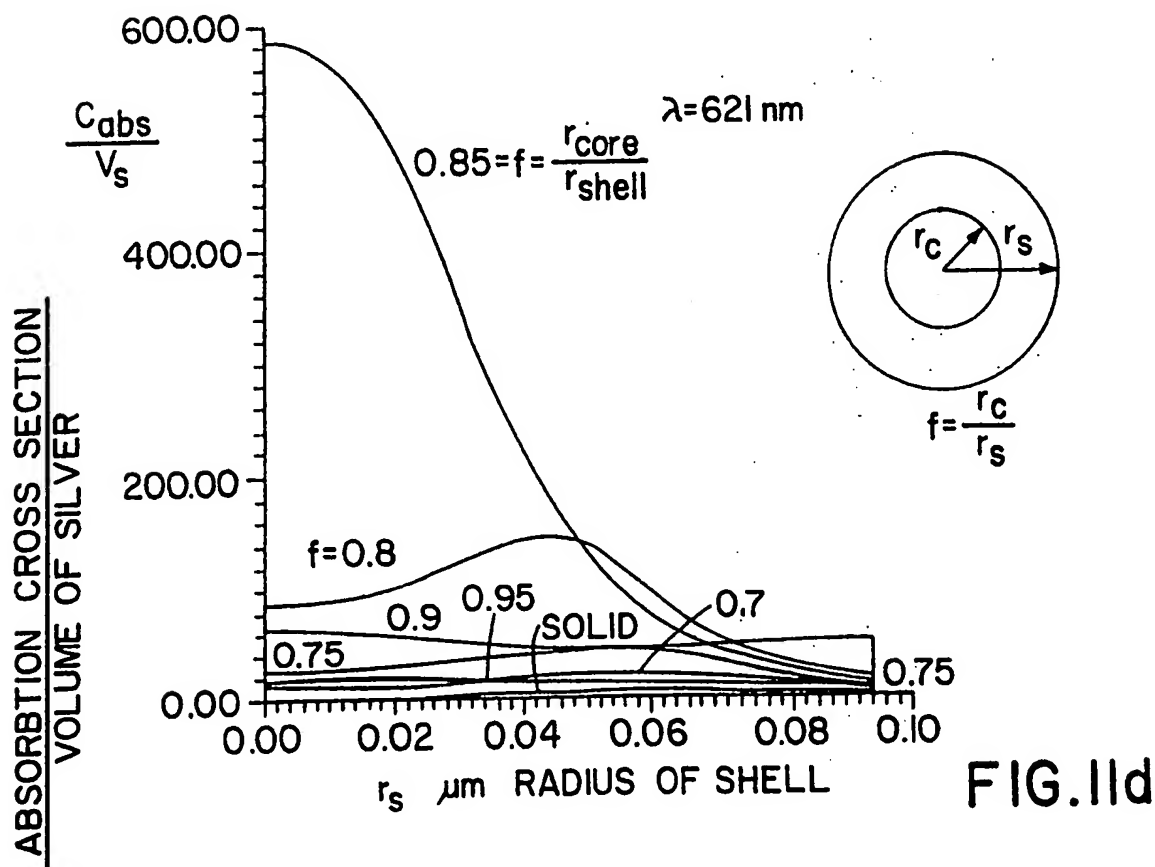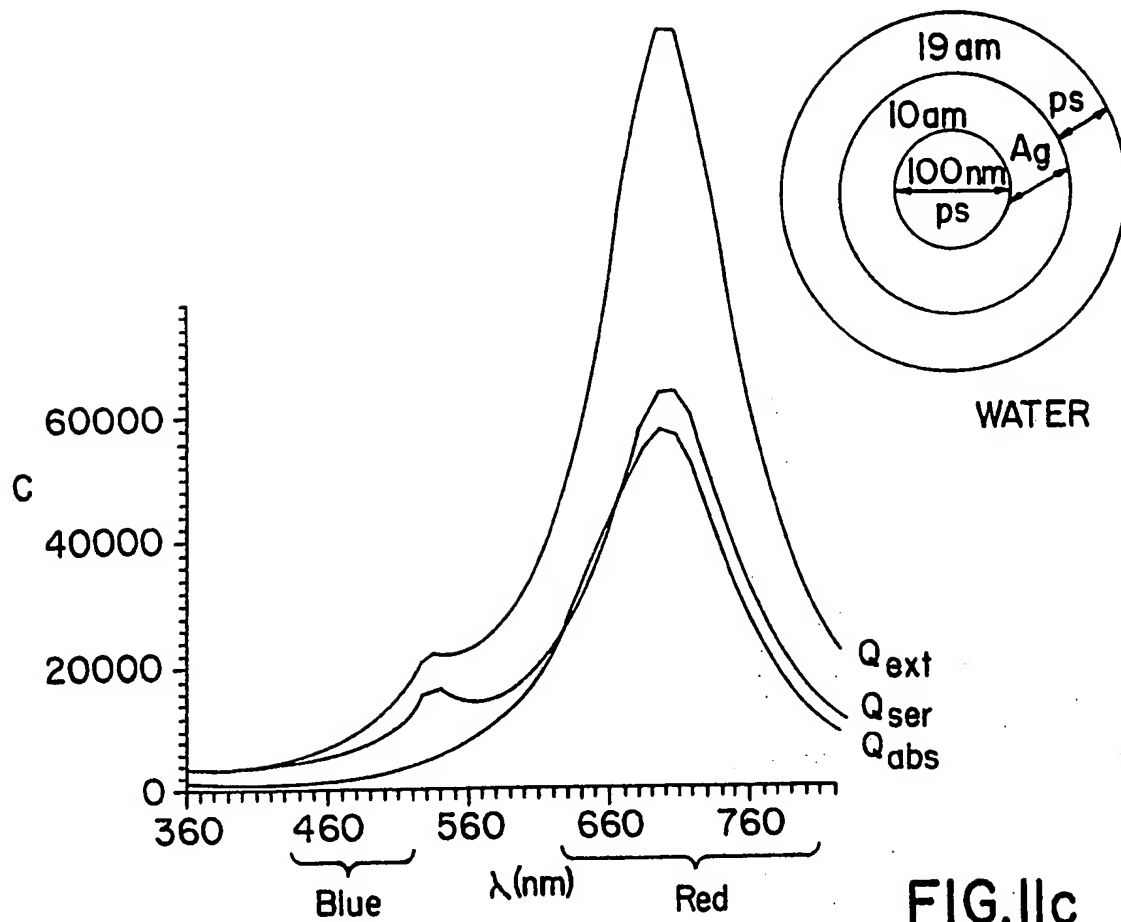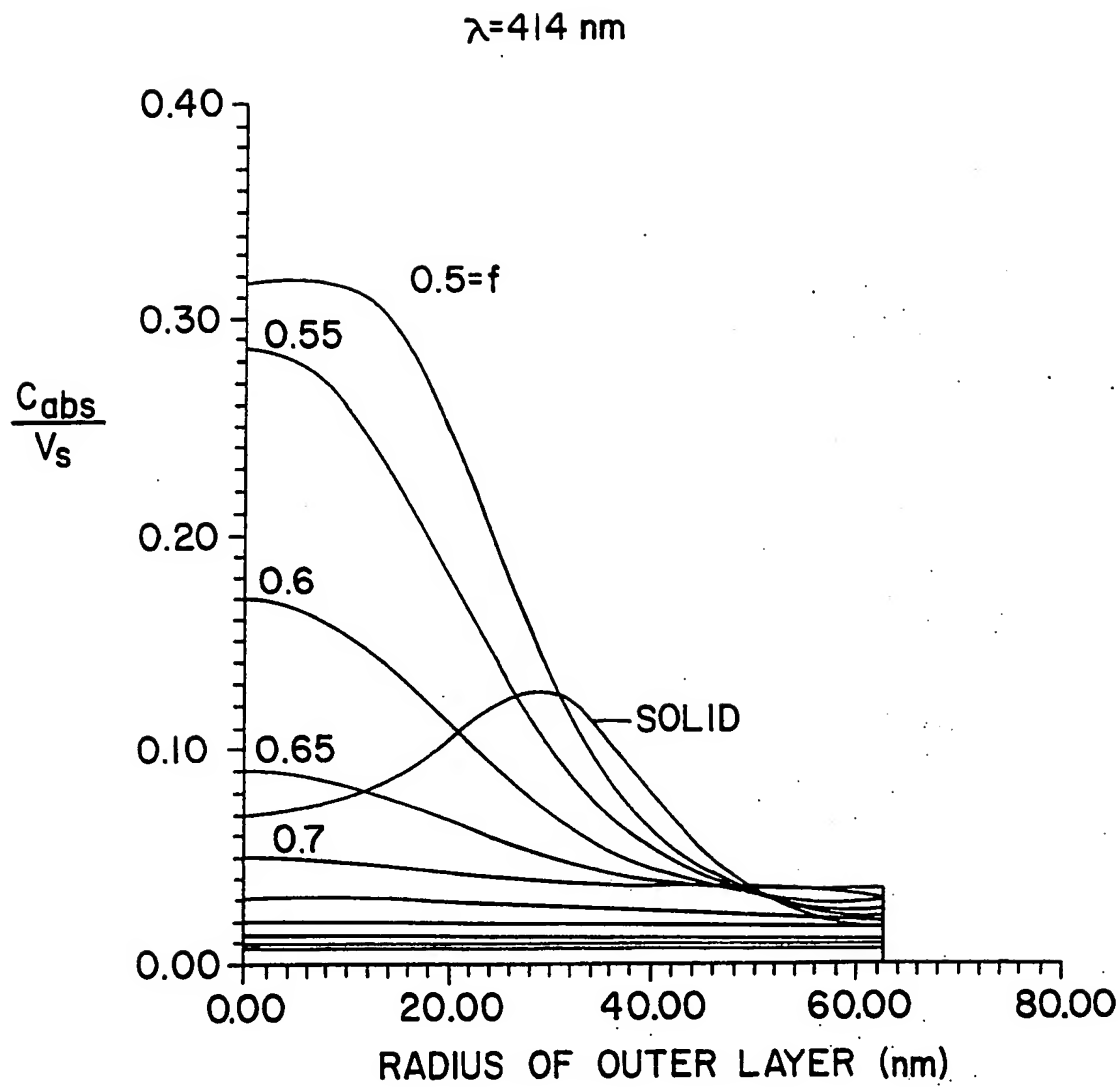
FIG.11e

Core=1.16 v.v.
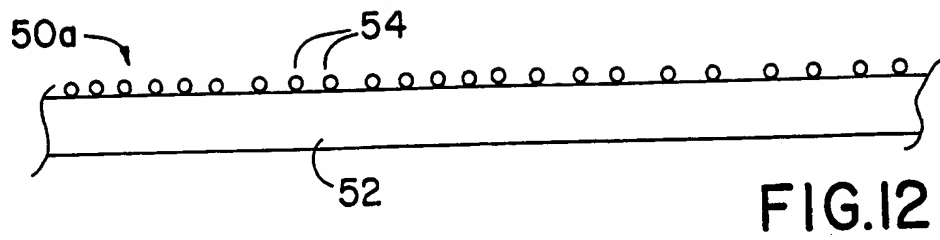Coat=Ag   O(0.5)5nm
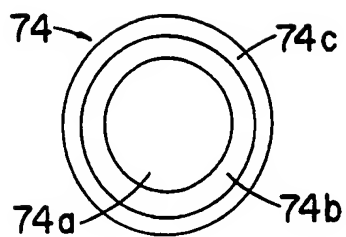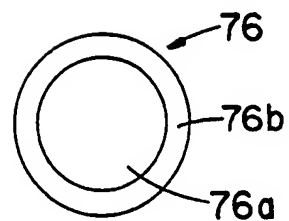Surround=water

t=O(0.5)5 nm

FIG.IIf

FIG.12

FIG.13

FIG.14

FIG.15

FIG.16

FIG.17

FIG.18

FIG.19
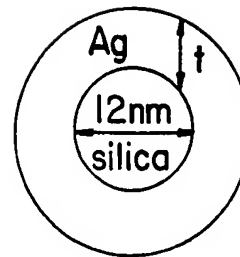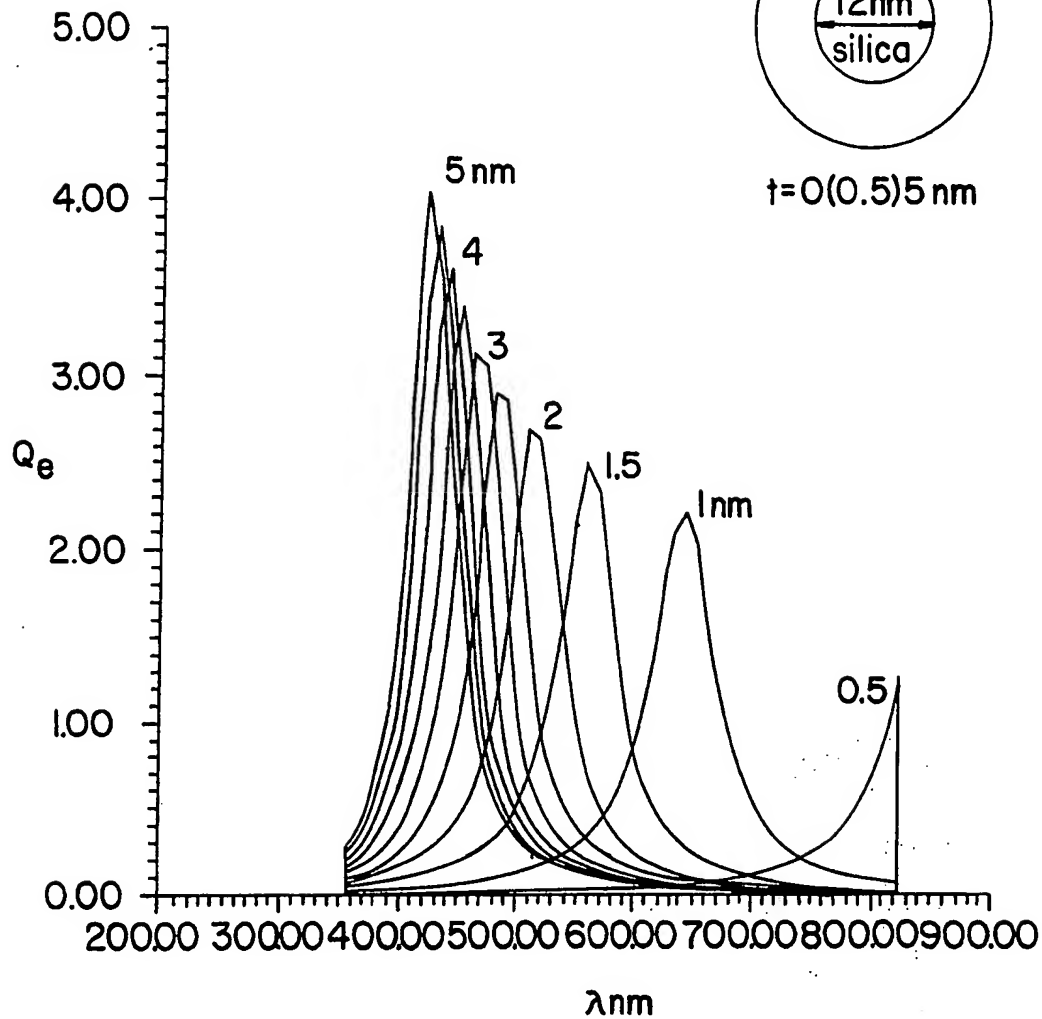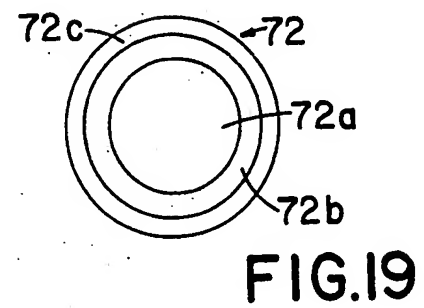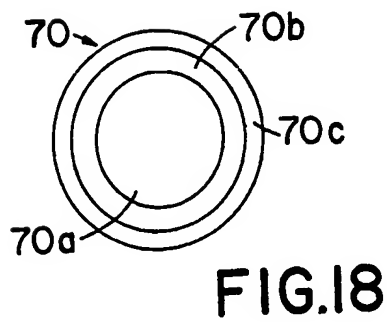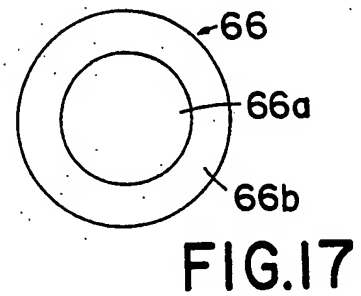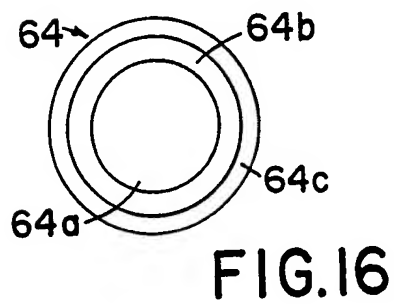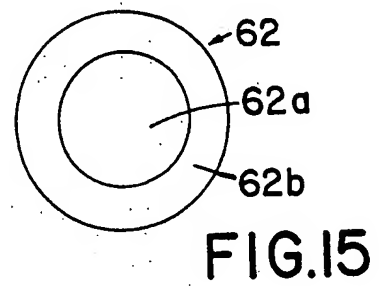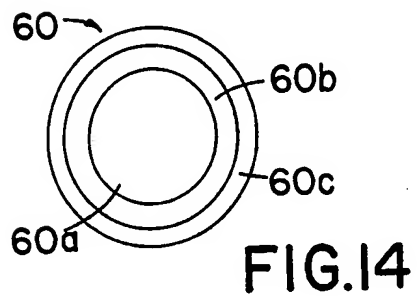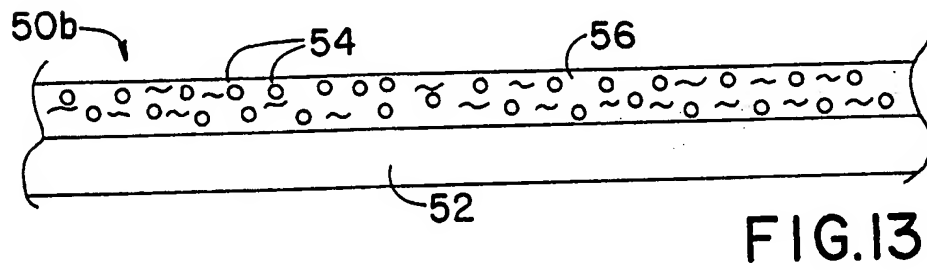
FIG.20

FIG.21
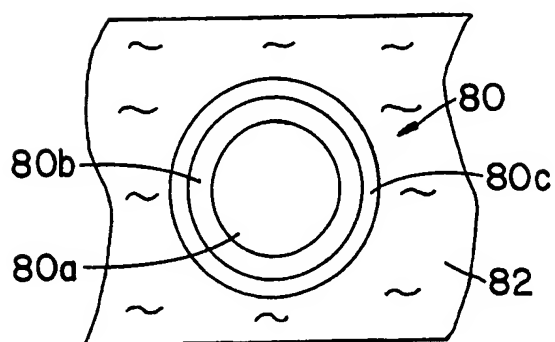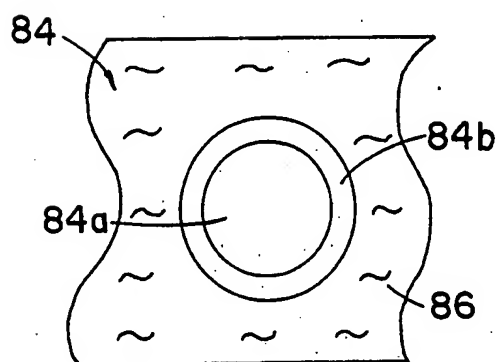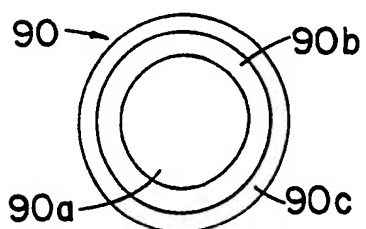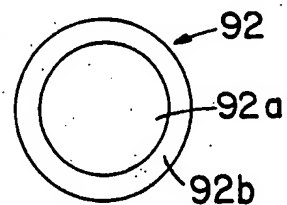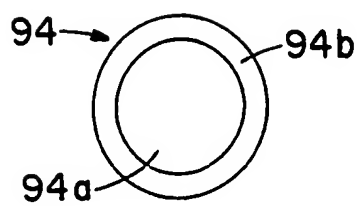
FIG.22

FIG.23

FIG.24

FIG.25

FIG.26
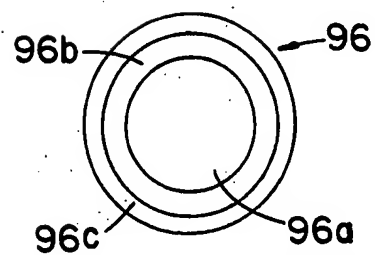
FIG.27

PROVIDE SOLUTION INCLUDING
DIELECTRIC PARTICLES, SILVER
IONS AND A HALIDE

REACT THE HALIDE WITH
THE SILVER IONS TO GROW
SILVER HALIDE COATINGS
OVER THE DIELECTRIC PARTICLES

FIG. 28

PROVIDE SOLUTION INCLUDING
DIELECTRIC PARTICLES, METAL
IONS, ISOPROPYL AND
ACETONE

REMOVE OXYGEN FROM
THE SOLUTION

EXPOSE THE SOLUTION TO
ULTRAVIOLENT LIGHT TO FORM
METAL COATING OVER THE
DIELECTRIC PARTICLES

FIG. 29

PROVIDE SOLUTION INCLUDING
SILVER HALIDE COATED
DIELECTRIC PARTICLES

EXPOSE THE SOLUTION TO
LIGHT TO CHANGE THE
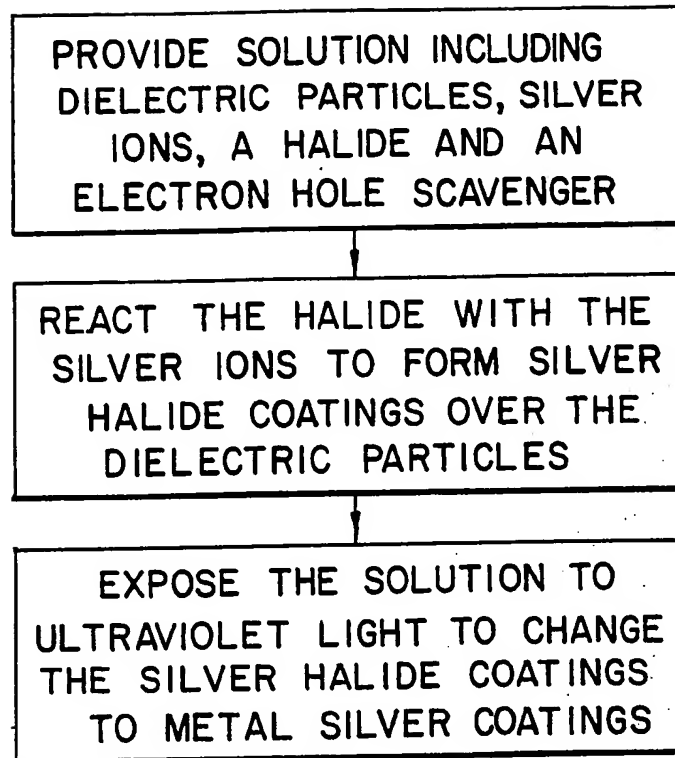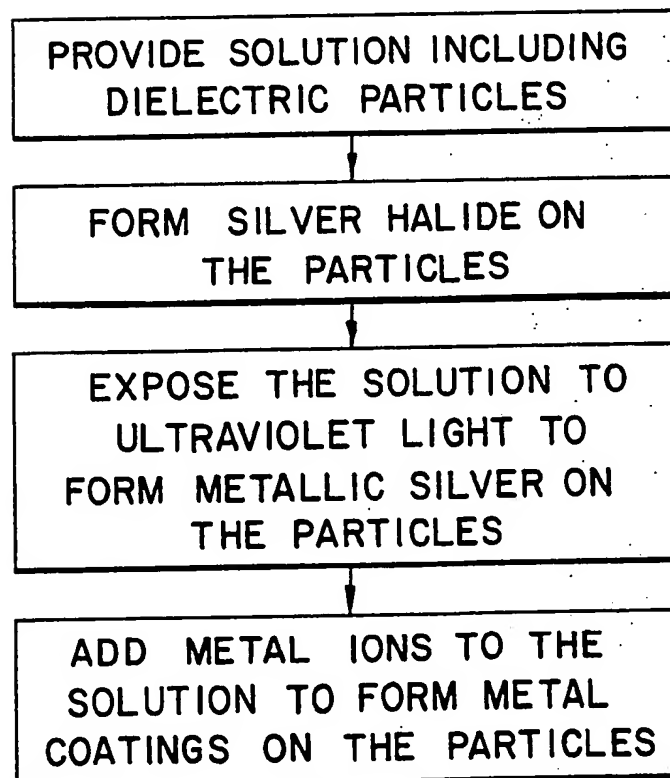SILVER HALIDE COATINGS
TO METAL SILVER COATINGS

FIG. 30

SUBSTITUTE SHEET

PROVIDE SOLUTION INCLUDING
DIELECTRIC PARTICLES, SILVER
IONS, A HALIDE AND AN
ELECTRON HOLE SCAVENGER

REACT THE HALIDE WITH THE
SILVER IONS TO FORM SILVER
HALIDE COATINGS OVER THE
DIELECTRIC PARTICLES

EXPOSE THE SOLUTION TO
ULTRAVIOLET LIGHT TO CHANGE
THE SILVER HALIDE COATINGS
TO METAL SILVER COATINGS

FIG.31

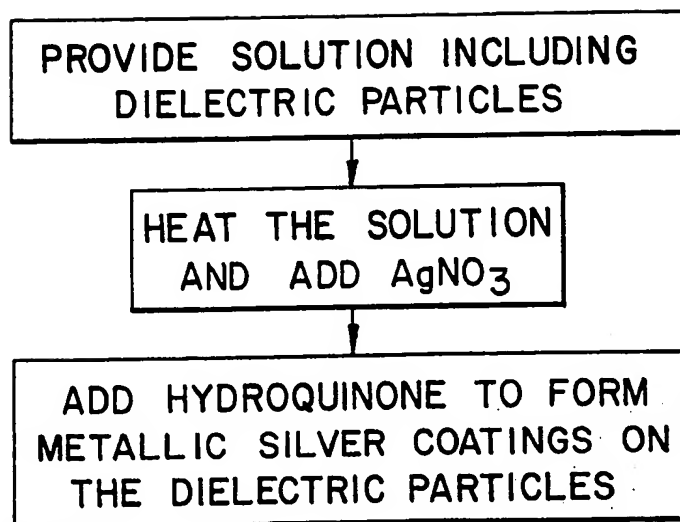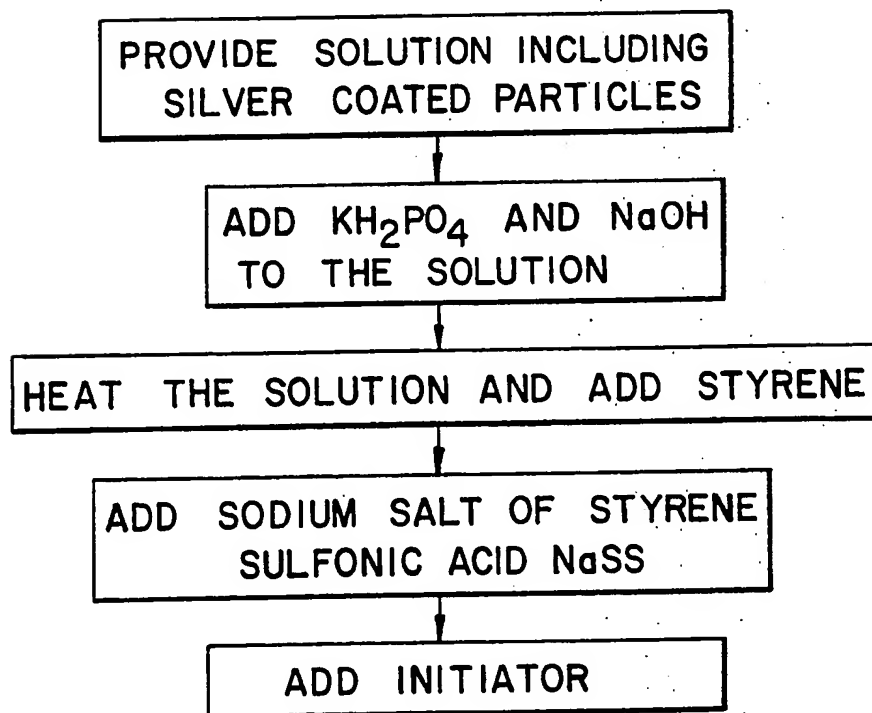PROVIDE SOLUTION INCLUDING
DIELECTRIC PARTICLES

FORM SILVER HALIDE ON
THE PARTICLES

EXPOSE THE SOLUTION TO
ULTRAVIOLET LIGHT TO
FORM METALLIC SILVER ON
THE PARTICLES

ADD METAL IONS TO THE
SOLUTION TO FORM METAL
COATINGS ON THE PARTICLES

FIG.32

PROVIDE SOLUTION INCLUDING
DIELECTRIC PARTICLES

HEAT THE SOLUTION
AND ADD AgNO$_3$

ADD HYDROQUINONE TO FORM
METALLIC SILVER COATINGS ON
THE DIELECTRIC PARTICLES

FIG.33

PROVIDE SOLUTION INCLUDING
SILVER COATED PARTICLES

ADD KH$_2$PO$_4$ AND NaOH
TO THE SOLUTION

HEAT THE SOLUTION AND ADD STYRENE

ADD SODIUM SALT OF STYRENE
SULFONIC ACID NaSS

ADD INITIATOR

FIG.34

```
┌─────────────────────────────┐
│   START  WITH DIELECTRIC     │
│        PARTICLES             │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│  FORM  METAL  COATINGS OVER  │
│  THE  DIELECTRIC  PARTICLES  │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│   FORM  SILVER  HALIDE       │
│   COATINGS OVER THE          │
│   METAL COATINGS             │
└─────────────────────────────┘
```

FIG.35

```
┌─────────────────────────────┐
│   START  WITH DIELECTRIC     │
│        PARTICLES             │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│  FORM  METAL  COATINGS OVER  │
│  THE  DIELECTRIC  PARTICLES  │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│   FORM  POLYMER COATINGS     │
│  OVER  THE  METAL COATINGS   │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│   FORM SILVER  HALIDE        │
│   COATINGS OVER  THE         │
│   POLYMER COATINGS           │
└─────────────────────────────┘
```

FIG.36

30 nm

FIG. 37

20 nm

FIG.38

FIG. 39

FIG. 40

FIG. 41

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): G03C 1/00,1/72; G11B 5/00,7/00; B05D 7/00; B32B 5/16, 9/00,15/02 U.S. CL. 430/138; 369/13,283; 427/217,221

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
U.S.	430/138, 567; 369/13, 280, 283, 284, 286, 288 427/217, 221; 428/402.24, 403, 404, 406, 407

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
Y	US, A, 4,587,533 (NAKANE ET AL) 06 MAY 1986; See column 1, lines 16-24.	1-33
Y	US, A, 4,770,973 (KANDA ET AL) 13 SEPTEMBER 1988; See column 1, lines 48-50.	1-33
Y	JP, A, 63-244424 (TOSHIBA CORP.) 11 OCTOBER 1988; See abstract.	1-33
Y	JP, B, 1-25149 (SHARP KK) 16 MAY 1989 See abstract.	1-33
Y	JP, A, 1-189049 (NEC CORP.) 28 JULY 1989 See abstract.	1-33

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
04 DECEMBER 1990	04 FEB 1991

International Searching Authority	Signature of Authorized Officer
ISA/US	Hoa V. Le

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET	

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers   . because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers   . because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

3. ☐ Claim numbers_____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

    I. Claims 1-16, 20-24 drawn to a microcapsule, classified
       in Class 430 Subclass 138.

    II. Claims 17-19 and 25-33 drawn to a method of storing and
        recording, classified in Class 369 Subclass 13.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.   Telephone Practice

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (supplemental sheet (2) (Rev. 11-87)

Con't. from Form PCT/ISA/210 supplemental sheet:

Group I, claims 1-16 and 20-24, which relates to micro-capsules containing a light sensitive silver halide.

Group II, contains claims 17-19 and 25-33. Claims 17-19 relate to magnetized sensitive metal. Claims 25-33 relate to a method of storing and reading data using the material of claims 17-19.

Applicant has not provided any evidence that the silver halide containing microcapsules as claimed in claim 1 are magnetized and can be able to store or read a data. In the absence of demonstrating a single invention. The above groups of claim invention are lacking of unity under PCT Rule 13.

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